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Supporting Information

Biologically Active Heteroglycoclusters Constructed on a Pillar[5]arene-Containing [2]Rotaxane Scaffold

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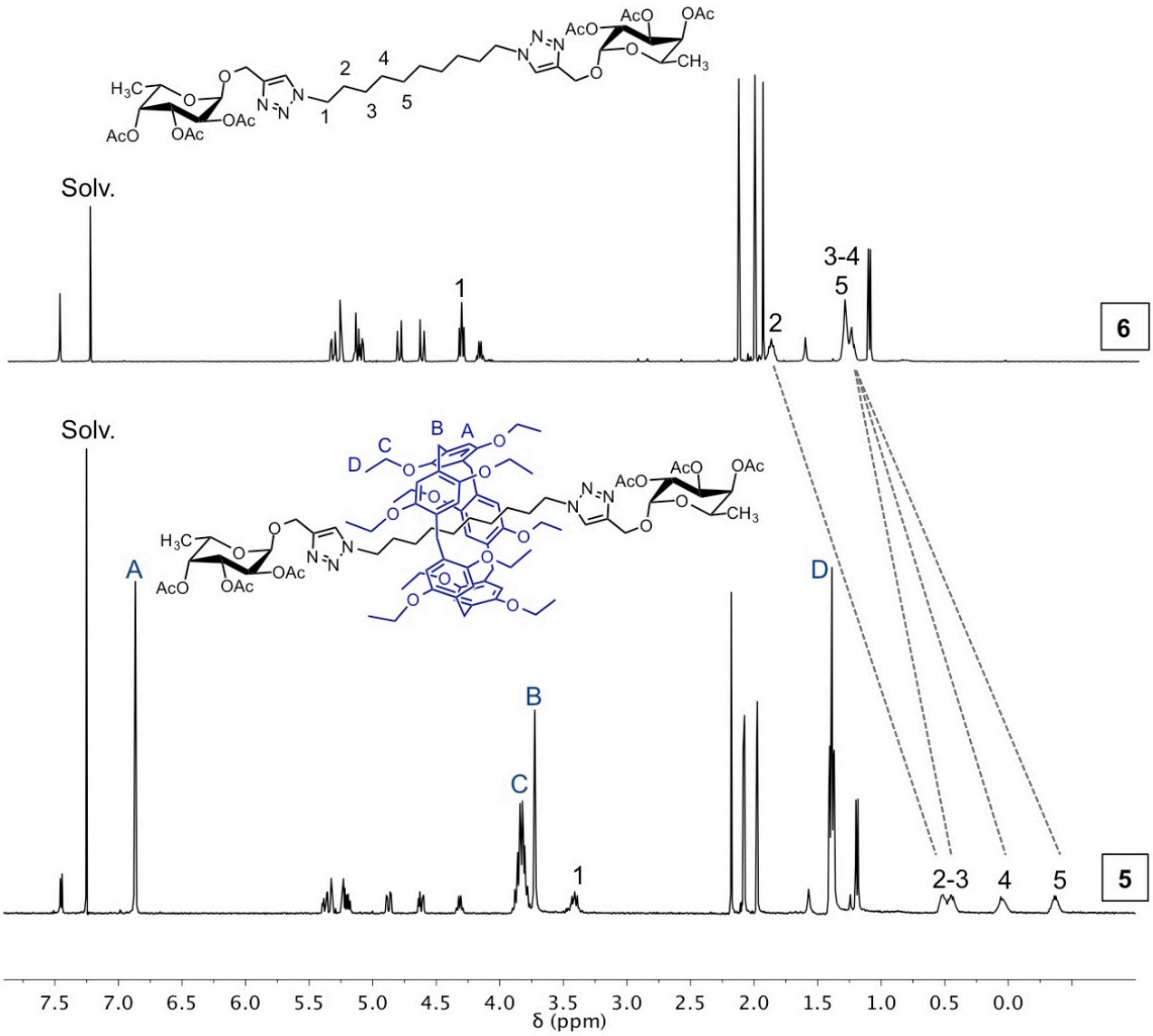


Figure S1. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compounds **5** and **6**.

As a result of the ring current effect of the pillar[5]arene aromatic subunits on the -$(CH_2)_{10}$- chain of the axle, the signals of protons H(2-5) are dramatically shielded in **5** when compared to the corresponding signals in **6**.

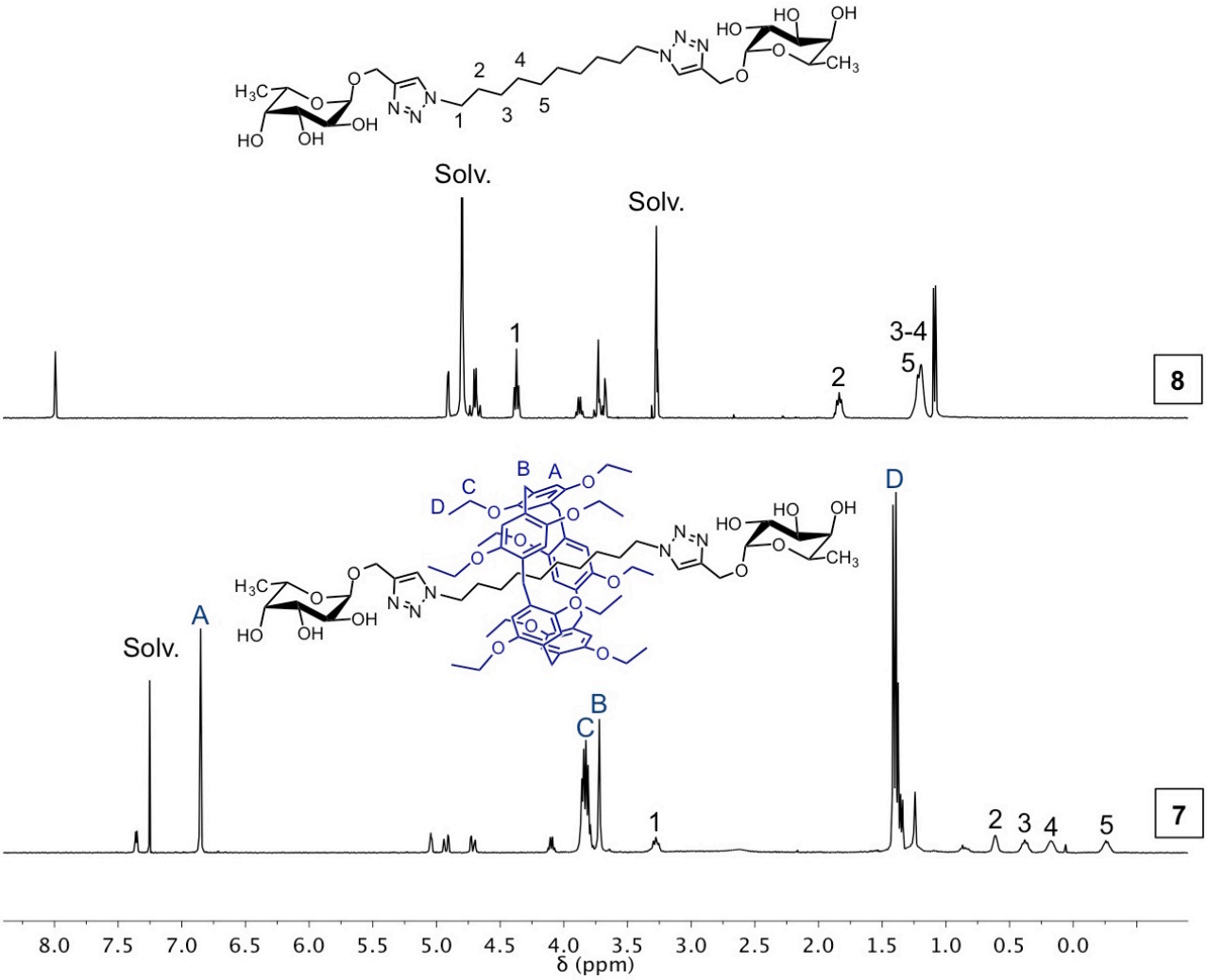


Figure S2. ^{1}H NMR spectra of compounds **7** (400 MHz, $CDCl_3$) and **8** (400 MHz, D_2O/CD_3OD 1:1).

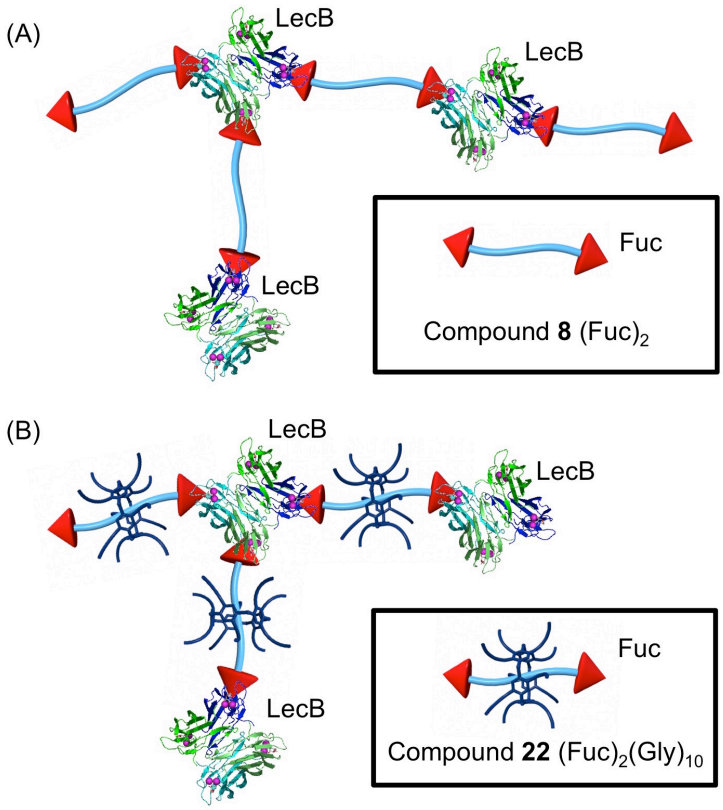


Figure S3. Schematic representation showing the aggregation of LecB to divalent ligands **8** (A) and **22** (B). Comparison of the K_D values (112 nM for **8** and 212 nM for **22**) reveals only limited steric effects resulting from the presence of the macrocyclic component in rotaxane **22**.

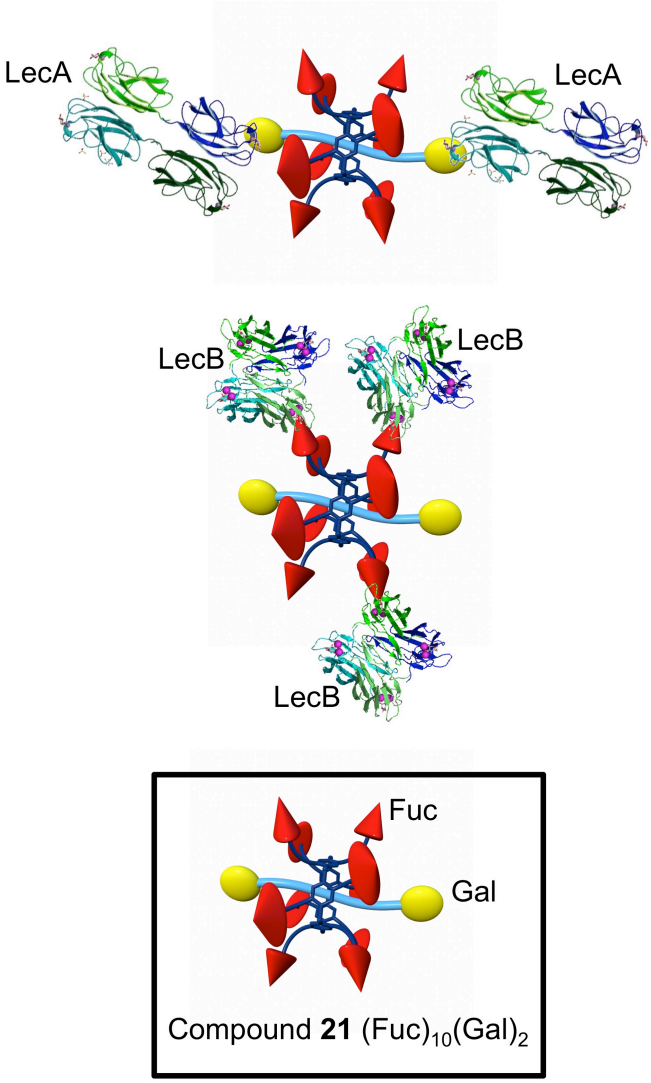
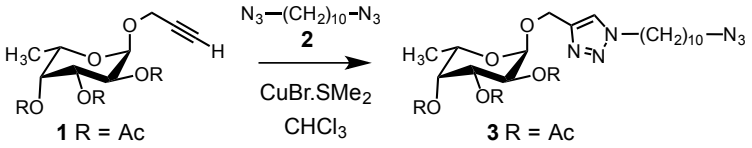


Figure S4. Schematic representation showing the aggregation of both LecA and LecB to ligand **21**. The macrocylic subunit prevents the clustering of the Gal moieties of the axle to LecA and thus the affinity of rotaxane **21** for LecA is moderate.

Synthesis

General methods. Reagents were purchased as reagent grade and used without further purification. Compounds **1**,[1] **2**,[2] **4**,[3] **9**,[4] **10**[5] and **25**[6] were prepared according to previously reported procedures. Acetonitrile (CH_3CN) was distilled over CaH_2 under Ar. Dichloromethane (CH_2Cl_2) was distilled over CaH_2 under Ar. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 F_{254} purchased from E. Merck. NMR spectra were recorded on a JEOL (ECX-400) spectrometer at 400MHz for proton resonance and at 100.4 MHz for carbon resonance. chemical shifts in ppm are given referred to the deuterated solvent used for the sampling (7.26 for $CDCl_3$, 4.79 for D_2O, 3.31 for MeOH-d_4 and 2.50 for DMSO-d_6). The following abbreviations were used to defined the multiplicities: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, and their combinations. Data are reported as follow: chemical shift, multiplicity, coupling constant, integration and label. MS measurements were performed either on a Agilent 6200 series TOF spectrometer in positive/negative/APCI ESI mode or on a Waters QToF1 spectrometer in MALDI LD+ mode. IR spectra were recorded on a Perkin Elmer RX 1 FT-IR spectrometer. Subtraction of the background was performed before recording the spectra. Liquid samples were performed as a film between two sodium chloride chips, while solid samples were analyzed as potassium bromide pellets. Samples were measured in the frequency range 400-4000 cm^{-1}. Optical activities of chiral molecules were measured on a Perkin Elmer 241 spectrometer using a sodium lamp (589 nm) at room temperature.

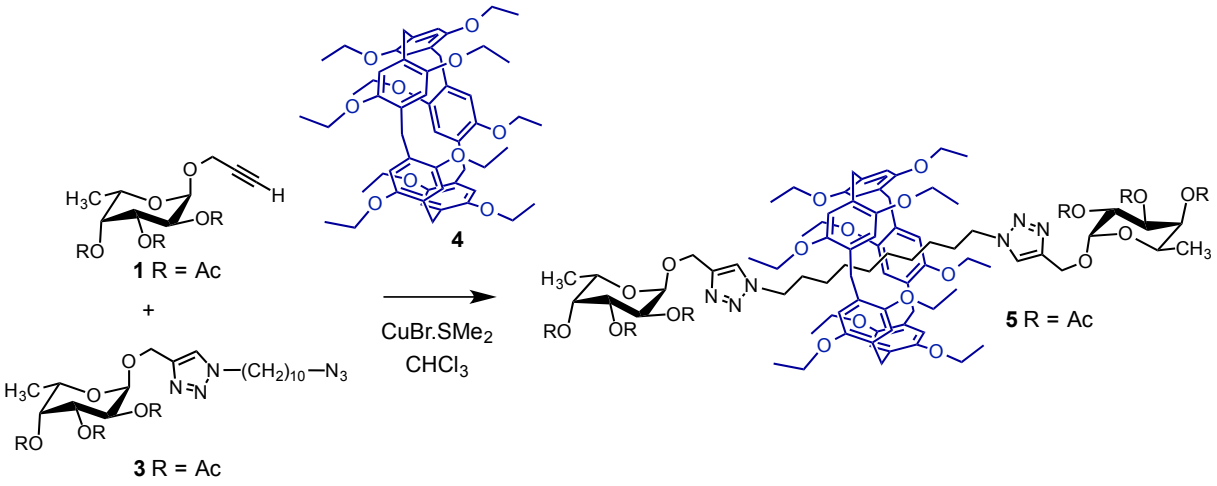
Compound 3



A mixture of **1** (300 mg, 0.91 mmol), **2** (612 mg, 2.74 mmol) and CuBr•SMe_2 (186 mg, 0.91 mmol) in dry $CHCl_3$ (3 mL) was stirred at room temperature during 3 h. The resulting solution was diluted

with CH_2Cl_2 (15 mL) and washed with a saturated NH_4Cl aqueous solution (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Column chromatography (SiO_2, Cy to Cy/EtOAc 1:1) gave **3** (380 mg, 75%) as a colorless oil. IR: 2097 (N_3), 1742 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (s, 1H), 5.36 (dd, J = 3.2 Hz, J = 10.8 Hz, 1H), 5.29 (d, J = 3.4 Hz, 1H), 5.18 (d, J = 3.7 Hz, 1H, H-1), 5.14 (dd, J = 3.7 Hz, J = 10.8 Hz, 1H), 4.84 (AB, J = 12.4 Hz, 1H), 4.66 (AB, J = 12.6 Hz, 1H), 4.35 (t, J = 7.3 Hz, 2H), 4.20 (q, J = 6.6 Hz, 1H), 3.26 (t, J = 7.1 Hz, 2H), 2.17 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.91 (t, J = 6.8 Hz, 2H), 1.57 (tt, J = 6.9 Hz, J = 7.1 Hz, 2H), 1.34-1.25 (m, 12H), 1.14 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.60, 170.36, 170.05, 143.91, 122.47, 95.67, 71.14, 68.01, 67.97, 64.69, 61.40, 51.45, 50.38, 30.35, 29.34, 29.25, 29.07, 28.97, 28.82, 26.68, 26.49, 20.83, 20.72, 20.68, 15.89. $[\alpha]_d$ ($CHCl_3$, c = 1.1, 20°C) = -83.4. Mass (TOF-MS-ESI$^+$): m/z: 575.28 (100%) $[M+Na]^+$, 591.25 (80%) $[M+K]^+$, 553..30 (50%) $[M+H]^+$. HRMS (TOF-MS-ESI$^+$, m/z): calculated for $C_{25}H_{40}N_3O_8Na$: 575.2800; found: 575.2801.

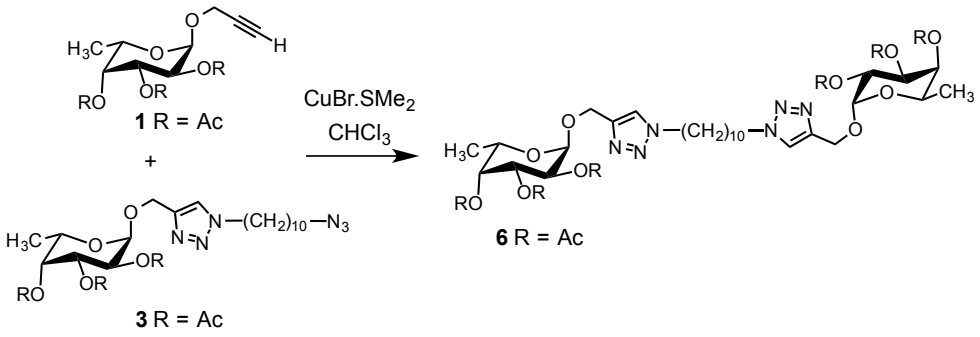
Compound 5



A solution of **4** (2.17 g, 2.44 mmol) and **3** (337 mg, 0.609 mmol) in dry $CHCl_3$ (3 mL) was stirred for two hours at room temperature. Afterwards **1** (240 mg, 0.732 mmol, 1.2 eq) was added and the solution was cooled to -20°C. CuBr•SMe_2 (125 mg, 0.609 mmol, 1 eq) was added and the resulting mixture stirred 15 h while warming slowly to room temperature. The solution was diluted with CH_2Cl_2 (20 mL) and washed with water (15 mL). The aqueous phase was extracted with CH_2Cl_2 (3x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (SiO_2, Cy to Cy/EtOAc 1:1) gave **5** (807 mg, 75%) as a colorless glassy product. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 and 7.45 (2s, 2H), 6.88 (s, 10H),

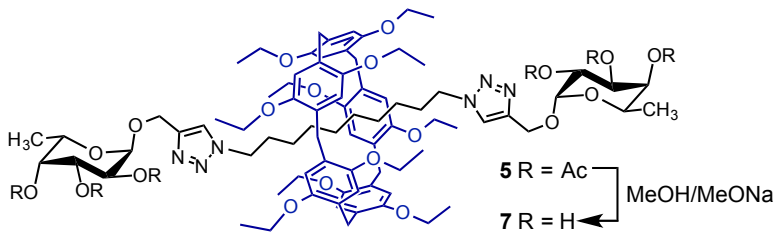
5.40-5.39 (m, 2H), 5.33 (bs, 2H), 5.24-5.18 (m, 4H), 4.89 (dd, J = 3.7 Hz, J = 11.7 Hz, 2H), 4.62 (dd, J = 3.9 Hz, J = 11.9 Hz, 2H), 4.32 (q, J = 6.6 Hz, 2H), 3.91-3.79 (m, 20H), 3.73 (s, 10H), 3.42 (t, J = 7.8 Hz 4H), 2.19, 2.09, 2.08, 1.99 and 1.98 (5s, 18H), 1.20 (d, J = 6.6 Hz, 6H), 0.53 (bs, 4H), 0.46 (bs, 4H), 0.06 (bs, 4H), -0.35 (bs, 4H).[13]C NMR (100 MHz, $CDCl_3$) δ = 170.68, 170.39, 170.05, 149.67, 142.94, 128.59, 122.43, 122.37, 114.52, 95.88, 71.23, 68.11, 68.02, 64.76, 63.71, 61.25, 50.00, 30.54, 29.34, 29.22, 29.07, 28.96, 25.85, 20.93, 20.76, 16.02, 15.50. $[\alpha]_d$ ($CHCl_3$, c = 1.1, 20°C) = -51.4. Mass (TOF-MS-ESI$^+$): m/z: 1771.91 (100%) $[M+H]^+$. HRMS (TOF-MS-ESI$^+$, m/z): calculated for $C_{95}H_{131}N_6O_{26}$: 1771.9108; found: 1771.9100.

Compound 6



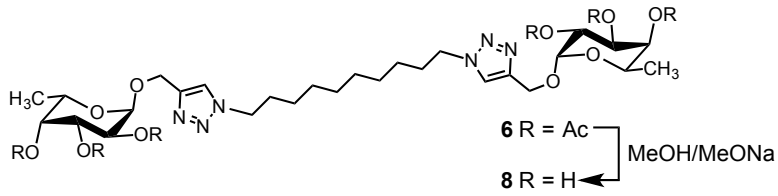
A mixture of **3** (83 mg, 0.15 mmol), **1** (59 mg, 0.18 mmol) and CuBr•SMe_2 (31 mg, 0.15 mmol) in dry $CHCl_3$ (2 mL) was stirred at room temperature during 15 h. The resulting solution was diluted with CH_2Cl_2 (15 mL) and washed with a saturated aqueous solution of NH_4Cl (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (SiO_2, Cy to Cy/EtOAc 3:7) gave **6** (82 mg, 62%) as a colorless powder. [1]H NMR (400 MHz, $CDCl_3$) δ = 7.50 (s, 2H), 5.35 (dd, J = 3.4 Hz, J = 10.8 Hz, 2H), 5.30-5.28 (m, 2H), 5.18 (d, J = 3.9 Hz, 2H), 5.13 (dd, J = 3.7 Hz, J = 10.8 Hz, 2H), 4.83 (AB, J = 12.6 Hz, 2H), 4.65 (AB, J = 12.4 Hz, 2H), 4.34 (t, J = 7.3 Hz, 4H), 4.20 (q, J = 6.6 Hz, 2H), 2.16, 2.03 and 1.97 (3s, 18H), 1.90 (tt, J = 6.9 Hz, J = 7.1 Hz, 4H), 1.32-1.27 (m, 12H), 1.13 (d, J = 6.6 Hz, 6H). [13]C NMR (100 MHz, $CDCl_3$) δ = 170.68, 170.44, 170.14, 144.01, 122.47, 95.76, 71.19, 68.08, 68.02, 64.76, 61.47, 50.44, 30.39, 29.29, 28.98, 26.53, 20.90, 20.78, 20.74, 15.93. Mass (TOF-MS-ESI$^+$): m/z: 903.40 (100%) $[M+Na]^+$. HRMS (TOF-MS-ESI$^+$, m/z): calculated for $C_{40}H_{60}N_6O_{16}Na$: 903.3958; found: 903.3987.

Compound 7



To a solution of **5** (103 mg, 0.058 mmol) in MeOH/CH_2Cl_2 2:1 (1.5 mL) at 0°C was added sodium methoxide (6 mg, 0.011 mmol). The resulting solution was stirred during two hours at 0°C. The solution was then filtered over a short column of Dowex™ 50WX8-200 (H^+ resin form). The resin was washed with methanol (10 mL) and water (10 mL) and finally solvents were evaporated under reduced pressure to afford **7** as colorless solid (75 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 and 7.36 (2s, 2H), 6.86 (s, 10H), 5.05 (s, 2H), 4.93 (dd, J = 2.1 Hz, J = 12.6 Hz, 2H), 4.72 (dd, J = 3.0 Hz, J = 12.6 Hz, 2H), 4.10 (q, J = 6.6 Hz, 2H), 3.86-3.80 (m, 26H), 3.73 (s, 10H), 3.29 (t, J = 7.8 Hz, 4H), 1.42-1.35 (m, 36H, 10CH_3), 0.62 (bs, 4H), 0.41-0.37 (m, 4H), 0.18 (bs, 4H), -0.25 (bs, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.70, 143.00, 128.75, 122.02, 114.69, 98.60, 71.80, 71.30, 69.44, 66.54, 63.85, 61.17, 61.12, 50.07, 30.60, 29.24, 28.74, 26.04, 16.40, 15.55. Mass (TOF-MS-ESI$^+$): m/z: 1519.85 (100%) $[M+H]^+$, 1541.83 (25%) $[M+Na]^+$ HRMS (TOF-MS-ESI$^+$, m/z): calculated for $C_{83}H_{119}N_6O_{20}$: 1519.8474; found: 1519.8474; calculated for $C_{83}H_{118}N_6O_{20}Na$: 1541.8293; found: 1541.8291.

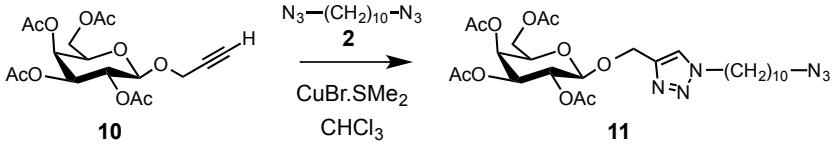
Compound 8



To a solution of **6** (20 mg, 0.023 mmol) in MeOH (0.3 mL) was added sodium methoxide (1.2 mg, 0.023 mmol). The resulting solution was stirred during two hours at room temperature. The solvent was evaporated and the crude was dissolved in water (0.5 mL). Amberlyst 15™ (0.5 g, previously washed with 1M HCl and water) was added to the solution and the mixture stirred for 2 min. Filtration and evaporation afforded **8** (12 mg, 84%) as a colourless solid. ^{1}H NMR (400 MHz,

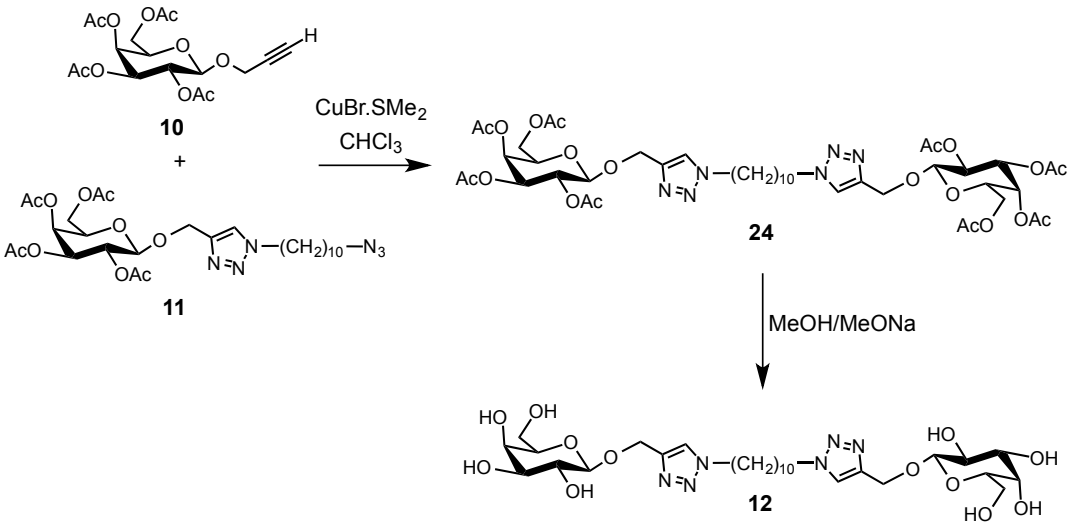
D_2O/MeOD 1:1) δ = 7.98 (s, 2H), 4.90 (d, J = 3.2 Hz, 2H), 4.71 (AB, J = 12.8 Hz, 2H), 4.66 (AB, J = 12.8 Hz, 2H), 4.36 (t, J = 6.9 Hz, 4H), 3.87 (q, J = 6.6 Hz, 2H), 3.72 (m, 4H), 3.67 (m, 2H), 1.83 (tt, J = 7.1 Hz, J = 7.1 Hz, 4H), 1.21-1.18 (m, 12H), 1.08 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, D_2O/MeOD 1:1) δ = 125.92, 100.26, 73.43, 71.29, 69.65, 68.17, 62.13, 51.79, 31.12, 30.11, 29.75, 27.24, 16.75. TOF-MS-ESI$^+$: m/z: 651.33 (100%) $[M+Na]^+$. HRMS (TOF-MS-ESI$^+$, m/z): calculated for $C_{28}H_{48}N_6O_{10}Na$: 651.3324; found: 651.3309.

Compound 11



A mixture of **10** (382 mg, 0.99 mmol), **2** (666 mg, 2.97 mmol) and CuBr•SMe_2 (203 mg, 0.99 mmol) in dry $CHCl_3$ (4 mL) was stirred at room temperature during 24 h. The solution was diluted with CH_2Cl_2 (15 mL) and washed with a saturated NH_4Cl aqueous solution (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (SiO_2, Cy to Cy/EtOAc 1:1) gave **11** (374 mg, 62%) as a colorless oil. IR: 2095 (N_3), 1746 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (s, 1H), 5.40 (d, J = 3.4 Hz, 1H), 5.23 (dd, J = 8.0 Hz, J = 10.5 Hz, 1H), 5.02 (dd, J = 3.4 Hz, J = 10.5 Hz, 1H), 4.98 (AB, J = 12.4 Hz, 1H), 4.81 (AB, J = 12.4 Hz, 1H), 4.66 (d, J = 8.0 Hz, 1H), 4.34 (t, J = 7.3 Hz, 2H), 4.21-4.12 (m, 2H), 3.95 (t, J = 6.6 Hz, 1H), 3.26 (t, J = 7.1 Hz, 2H), 2.15, 2.06, 1.99 and 1.98 (4s, 12H), 1.90 (bs, 2H), 1.60-1.56 (m, 2H), 1.39-1.25 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.47, 170.28, 170.14, 169.56, 144.21, 122.52, 100.47, 70.87, 68.84, 67.11, 63.12, 61.35, 51.49, 50.44, 30.36, 29.37, 29.29, 29.11, 28.99, 28.85, 26.96, 26.71, 26.51, 20.82, 20.76, 20.73, 20.63. $[\alpha]_d$ ($CHCl_3$, c = 1.3, 20°C) = - 19.4. Mass (TOF-MS-ESI$^+$): m/z: 633.2860 (100%) $[M+Na]^+$, 649.2592 (95%) $[M+K]^+$, 611.3027 (60%) $[M+H]^{+\cdot}$ HRMS (TOF-MS-ESI$^+$, m/z): calculated for $C_{27}H_{43}N_6O_{10}$: 611.3035; found: 611.3027; calculated for $C_{27}H_{42}N_6O_{10}Na$: 633.2855; found: 633.2860; calculated for $C_{27}H_{42}N_6O_{10}K$: 649.2594; found: 649.2592.

Compound 12

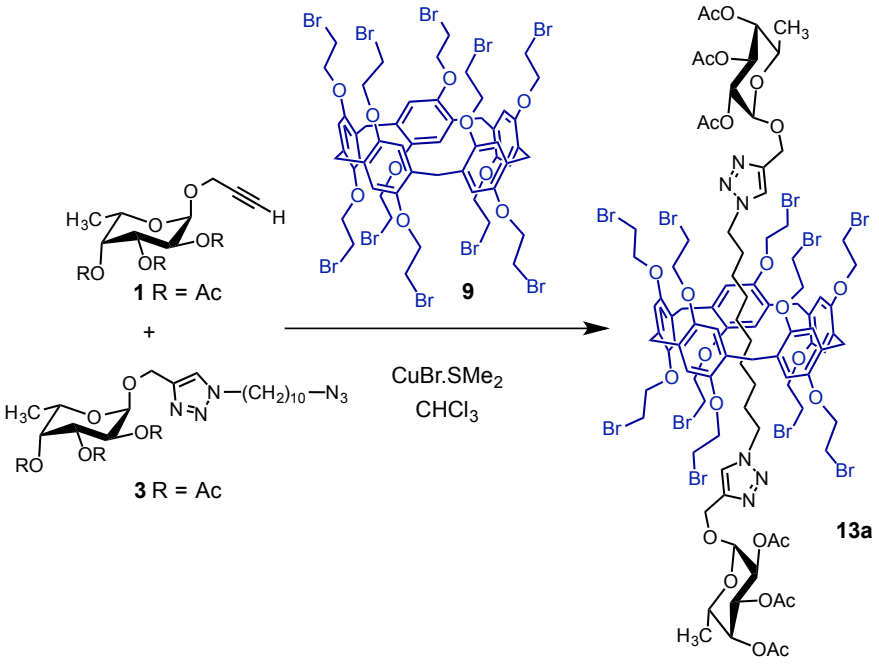


24. A mixture of **11** (65 mg, 0.11 mmol), **10** (50 mg, 0.13 mmol) and CuBr•SMe_2 (22 mg, 0.11 mmol) in dry $CHCl_3$ (1.5 mL) was stirred at room temperature. After 15 h, the solution was diluted with CH_2Cl_2 (15 mL) and washed with a saturated aqueous solution of NH_4Cl (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3x 10 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. Column chromatography (SiO_2, Cy to Cy/EtOAc 3:7) gave **24** (71 mg, 67%) as a colourless powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (s, 2H), 5.40 (d, J = 2.5 Hz, 2H), 5.22 (dd, J = 8.0 Hz, J = 10.3 Hz, 2H), 5.01 (dd, J = 3.4 Hz, J = 10.5 Hz, 2H), 4.97 (AB, J = 12.6 Hz, 2H), 4.81 (AB, J = 12.6 Hz, 2H), 4.66 (d, J = 8.0 Hz, 2H), (t, J = 7.6 Hz, 4H), 4.16 (m, 4H), 3.95 (t, J = 7.6 Hz, 2H), 2.15, 2.06, 1.99 and 1.98 (4s, 24H), 1.89 (t, J = 6.9 Hz, 4H), 1.31-1.26 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.49, 170.29, 170.16, 169.59, 144.30, 122.55, 100.54, 70.89, 68.87, 67.12, 63.18, 61.34, 50.46, 30.36, 29.27, 28.95, 26.49, 20.85, 20.79, 20.75, 20.66. TOF-MS-ESI$^+$: m/z: 1019.41 (100%) $[M+Na]^+$. HRMS (TOF-MS-ESI$^+$, m/z): calculated for $C_{44}H_{64}N_6O_{20}Na$: 1019.4068; found: 1019.4069.

12. To a solution of **24** (20 mg, 0.020 mmol) in MeOH (0.3 mL) was added sodium methoxide (1.1 mg, 0.020 mmol) and the solution was stirred during 2 h at room temperature. The solvent was evaporated and the residue dissolved in water (0.5 mL). Amberlyst 15™ (0.5 g, previously washed with 1M HCl and water) was then added. The resulting mixture was stirred for 2 min, then filtered and evaporated to afford **12** as colourless solid (12 mg, 91%). ^{1}H NMR (400 MHz, D_2O) δ = 8.03 (s, 2H), 4.97 (AB, J = 12.6 Hz, 2H), 4.84 (AB, J = 12.6 Hz, 2H), 4.44 (d, J = 7.8 Hz, 2H), 4.39 (t, J = 6.9 Hz, 4H), 3.90 (d, J = 3.4 Hz, 2H), 3.79-3.70 (m, 4H), 3.66 (dd, J = 4.6 Hz, J = 7.8 Hz, 2H),

3.60 (dd, J = 3.4 Hz, J = 9.9 Hz, 2H), 3.51 (dd, J = 7.8 Hz, J = 10.1 Hz, 2H), 1.85 (tt, J = 6.2 Hz, J = 7.1 Hz, 4H), 1.20-1.18 (m, 12H). ^{13}C NMR (100 MHz, D_2O) δ = 143.42, 125.26, 101.91, 75.21, 72.72, 70.62, 68.55, 61.81, 60.92, 50.47, 29.23, 28.20, 27.84, 25.38. TOF-MS-ESI$^+$: m/z: 683.32 (100%) $[M+Na]^+$. HRMS (TOF-MS-ESI$^+$, m/z): calculated for $C_{25}H_{40}N_3O_8Na$: 683.3227; found: 683.3203.

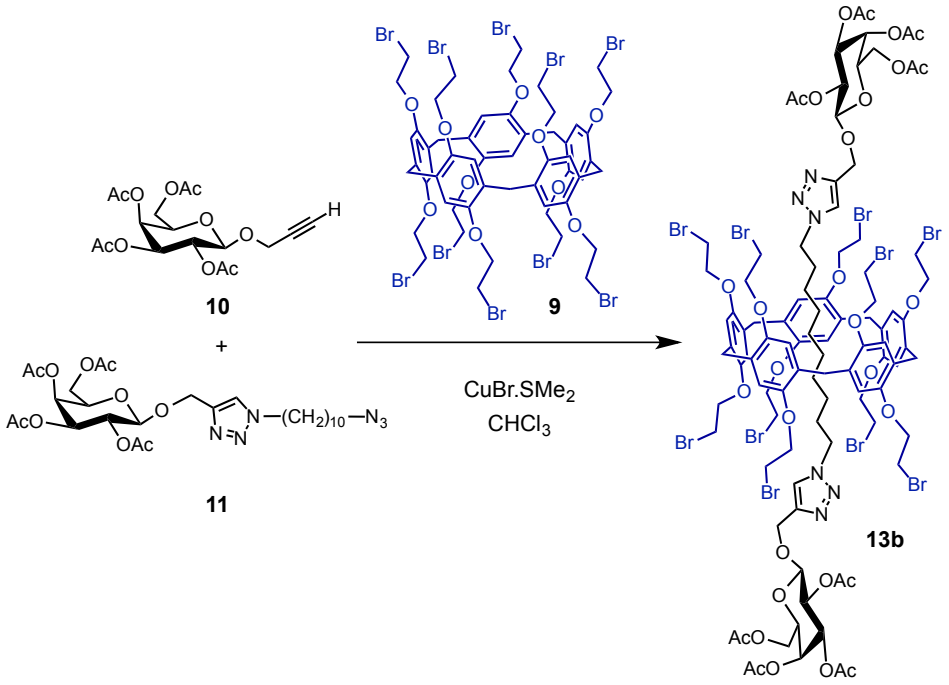
Compound 13a



A solution of **9** (1.51g, 0.89 mmol) and **3** (124 mg, 0.22 mmol) in dry $CHCl_3$ (3 mL) was stirred two hours at room temperature. Afterwards **1** (88 mg, 0.27 mmol, 1.2 eq) was added and the solution was cooled to -20°C. CuBr•SMe_2 (46 mg, 0.22 mmol) was added and the resulting mixture stirred 15h while warming slowly to room temperature. The solution was diluted with CH_2Cl_2 (10 mL) and washed with water (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (SiO_2, Cy to Cy/EtOAc 1:1) gave **13a** (182 mg, 32%) as a colorless glassy product. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 and 7.51 (2s, 2H), 7.00 (s, 10H), 5.42-5.37 (m, 2H), 5.34 (bs, 2H), 5.24-5.19 (m, 4H), 4.89 (dd, J = 2.1 Hz, J = 11.9 Hz, 2H), 4.67 (dd, J = 6.0 Hz, J = 12.1 Hz, 2H), 4.35-4.11 (m, 22H, 2H-5), 3.81 (s, 10H), 3.68 (t, J = 5.5 Hz, 20H), 3.62-3.49 (m, 4H), 2.18, 2.11, 2.09 and 1.98 (4s, 18H), 1.21 (d, J = 6.4 Hz, 3H), 1.20 (d, J = 6.4 Hz, 3H), 0.69 (bs, 4H), 0.31 (bs, 4H), -0.11 (bs, 4H), -0.27 (bs, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.71, 170.54, 170.45, 170.13, 149.77, 143.36, 129.40, 122.56, 115.98, 95.98, 95.87,

71.36, 71.28, 69.26, 69.21, 68.21, 68.08, 67.93, 64.87, 61.40, 61.35, 50.20, 31.21, 30.46, 29.72, 29.66, 29.21, 29.03, 26.01, 21.18, 21.12, 20.82, 16.07. Mass (MALDI-TOF-LD+): m/z: 2481.1 (100%) $[M-Br]^+$, 2561.0 (30%) $[M]^+$.

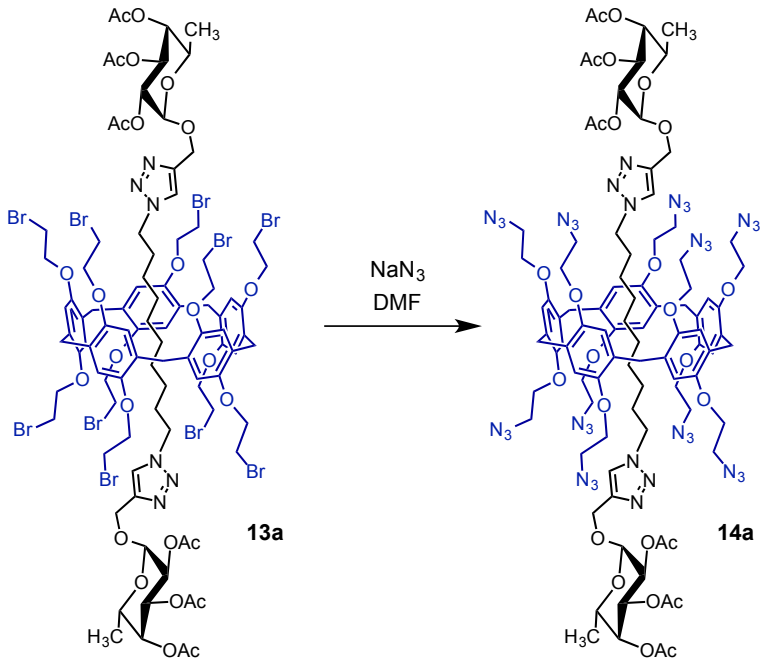
Compound 13b



A solution of **9** (1.04 g, 0.62 mmol) and **11** (94 mg, 0.15 mmol) in dry $CHCl_3$ (3 mL) was stirred three hours at room temperature. Afterwards **10** (71 mg, 0.19 mmol) was added and the solution was cooled to -20°C. CuBr•SMe_2 (37 mg, 0.22 mmol) was added and the resulting mixture stirred 15h while warming slowly to room temperature. The solution was diluted with CH_2Cl_2 (10 mL) and washed with water (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (SiO_2, Cy/CH_2Cl_2 then Cy/EtOAc 1:1) gave **13b** (108 mg, 26%) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 and 7.45 (2s, 2H), 7.01 and 7.00 (2s, 10H), 5.44 (d, J = 2.5 Hz, 2H), 5.30-5.23 (m, 2H), 5.10-5.06 (m, 4H), 4.80 (dd, J = 2.3 Hz, 11.7 Hz, 2H), 4.73 (t, J = 7.3 Jz, 2H), 4.30-4.11 (m, 24H), 4.01 (t, J = 6.6 Hz, 2H), 3.82 (s, 10H), 3.69 (t, J = 5.5 Hz, 20H), 3.42 (t, J = 8.5 Hz, 4H), 2.19, 2.09, 2.09 and 2.00 (4s, 24H), 0.55-0.48 (m, 8H), 0.04 (bs, 4H), -0.25 (bs, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.53, 170.34, 170.22, 169.68, 169.60, 149.76, 143.33, 129.41, 122.45, 115.94, 100.89, 100.68, 70.97, 69.18, 68.87, 67.18, 63.40, 63.24,

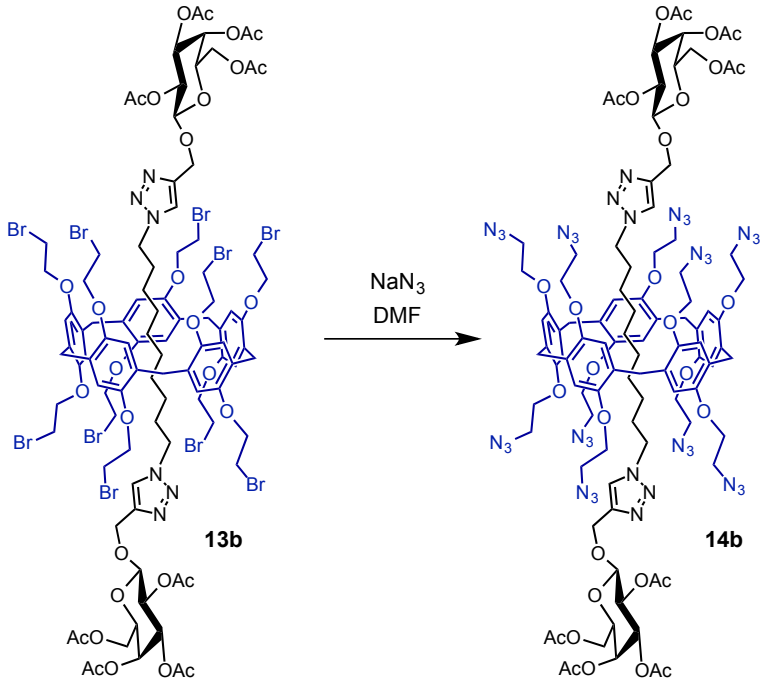
61.45, 61.33, 50.09, 31.28, 31.13, 30.60, 30.25, 29.39, 29.31, 29.01, 26.02, 21.07, 20.87, 20.70. Mass (MALDI-TOF-LD+): m/z: 2597.1 (100%) $[M-Br]^+$, 2677.0 (5%) $[M]^+$.

Compound 14a



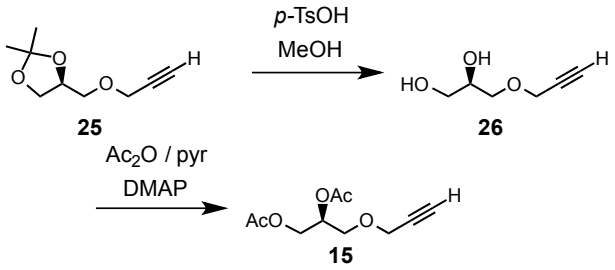
A mixture of **13a** (149 mg, 0.058 mmol) and NaN_3 (76 mg, 1.16 mmol) in dry DMF (2.5 mL) was stirred at room temperature during 24 h. The solution was diluted with Et_2O (10 mL) and washed with brine (3x 10 mL). The combined aqueous layers were extracted with Et_2O (3x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (SiO_2, Cy to Cy/EtOAc 1:1) gave **14b** (119 mg, 94 %) as a colorless oil. IR: 2094 (N_3), 1744 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 and 7.46 (2s, 2H), 6.94 (s, 10H), 5.41 (dd, J = 3.2 Hz, J = 10.1 Hz, 2H), 5.33 (d, J = 3.2 Hz, 2H), 5.25-5.19 (m, 4H), 4.88 (d, J = 11.9 Hz, 2H), 4.66 (dd, J = 2.1 Hz, J = 12.1 Hz, 2H), 4.31 (q, J = 6.9 Hz, 2H, 2H-5), 4.07-3.95 (m, 20H), 3.81 (s, 10H), 3.67 (t, J = 5.3 Hz, 20H), 3.54-3.45 (m, 4H), 2.19, 2.11, 2.08 and 1.99 (4s, 18H), 1.20 (d, J = 6.4 Hz, 6H), 0.63-0.59 (m, 4H), 0.37 (bs, 4H), -0.04 (bs, 4H), -0.23 (bs, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.71, 170.52, 170.17, 149.81, 143.39, 129.11, 122.49, 115.26, 95.83, 95.76, 71.30, 68.25, 68.17, 67.92, 67.87, 67.36, 67.32, 64.89, 61.07, 61.00, 51.39, 50.08, 30.48, 29.52, 29.11, 25.99, 20.92, 20.80, 16.01. Mass (MALDI-TOF-LD+): m/z: 2180.9 (100%) $[M]^+$, 2139.9 (95%) $[M-N_3]^+$. HRMS (MALDI-TOF-LD+, m/z): calculated for $C_{95}H_{120}N_{36}O_{26}$: 2180.9174; found: 2180.9182.

Compound 14b



A mixture of **13b** (103 mg, 0.038 mmol) and NaN_3 (50 mg, 0.77 mmol) in dry DMF (2 mL) was stirred at room temperature during 24 h. The solution was diluted with Et_2O (10 mL) and washed with brine (3x 10 mL). The combined aqueous layers were extracted with Et_2O (3x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (SiO_2, Cy to Cy/EtOAc 1:1) gave **14b** (75 mg, 85%) as a colorless oil. IR: 2093 (N_3), 1747 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (bs, 2H), 6.94 and 6.94 (2s, 10H), 5.45 (d, J = 3.2 Hz, 2H), 5.26 (m, 2H), 5.07 (m, 3H), 4.73 (m, 3H), 4.27-4.17 (m, 4H), 4.03-3.96 (m, 22H), 3.81 (s, 10H), 3.66 (bs, 20H), 3.37 (bs, 4H), 2.17 (s, 6H), 2.08 (s, 12H), 2.00 (s, 6H), 0.51 (bs, 8H), 0.07 (bs, 4H), -0.22 (bs, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.50, 170.29, 170.20, 169.60, 149.76, 143.43, 129.07, 122.45, 115.25, 115.18, 101.02, 100.89, 71.00, 68.86, 67.31, 67.15, 63.29, 63.20, 61.35, 61.28, 51.38, 51.35, 49.96, 30.57, 29.25, 29.20, 29.10, 26.05, 25.99, 20.91, 20.86, 20.79, 20.67. Mass (MALDI-TOF-LD+): m/z: 2255.9 (100%) $[M-N_3]^+$, 2296.9 (45%) $[M]^+$. HRMS (MALDI-TOF-LD+, m/z): calculated for $C_{95}H_{120}N_{36}O_{26}$: 2296.9284; found: 2296.9260.

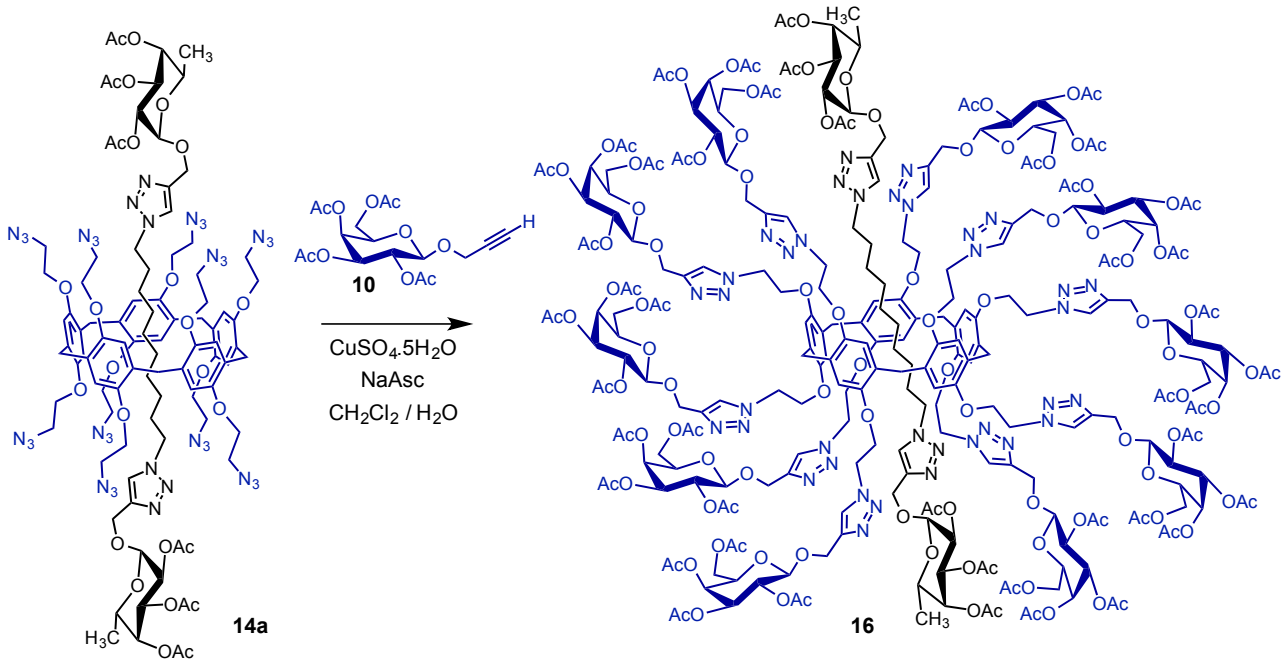
Compound 15



26. A solution of **25** (0.86 g, 5.07 10^{-3} mol) and *p*-toluenesulfonic acid (*p*-TsOH, 0.48 g, 2.53 10^{-3} mol) in MeOH (40 mL) was stirred at room temperature during 15 h. $NaHCO_3$ (2 g) was added to the solution. The resulting mixture was filtered and concentrated under reduced pressure. Column chromatography (SiO_2, Cy/EtOAc 1:1 to EtOAc) gave **26** (0.50 g, 76%) as a colorless liquid. ^1H NMR (400 MHz, D_2O) δ = 4.18 (d, J = 2.5 Hz, 2H), 3.90 (m, 1H), 3.69 (dd, J = 3.7 Hz, J = 10.5 Hz, 1H), 3.61-3.53 (m, 3H), 2.47 (t, J = 2.3 Hz, 1H). ^{13}C NMR (100 MHz, D_2O) δ = 79.37, 75.11, 71.40, 70.77, 63.90, 58.73. $[\alpha]_d$ ($CHCl_3$, c = 1, 20°C) = + 1.2. Mass (TOF-MS-ESI$^+$): m/z: 153.0519 (100%) $[M+Na]^+$. HRMS (TOF-MS-ESI$^+$, m/z): calculated for $C_6H_{10}O_3Na^+$: 153.0522; found: 153.0519.

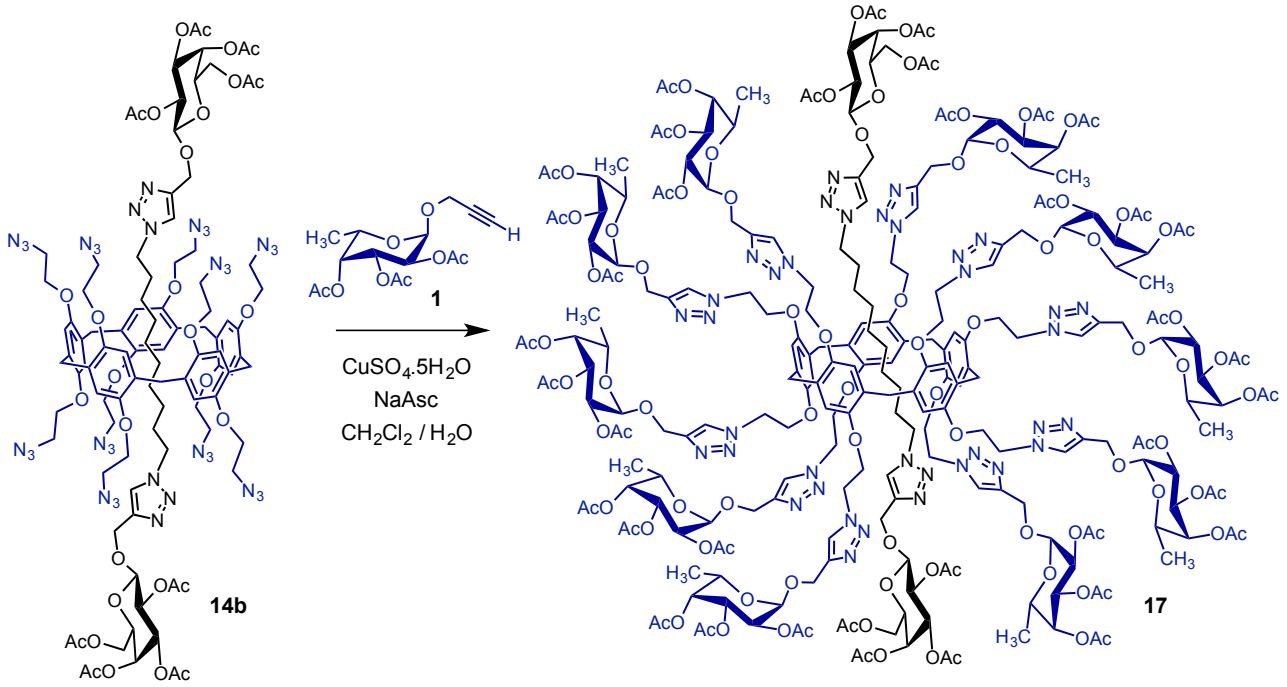
15. Acetic anhydride (1.43 mL, 14.3 mmol) was added to a solution of **26** (465 mg, 3.57 mmol) and *N,N*-dimethylaminopyridine (DMAP, 43 mg, 0.36 mmol) in dry pyridine (pyr, 10 mL) at room temperature. After 30 min, the solution was diluted with EtOAc (20 mL) and washed with a 1 M HCl aqueous solution (3x 10 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (SiO_2, Cy to Cy/EtOAc 1:1) gave **15** (566 mg, 74%) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ = 5.21 (tt, J = 5.0 Hz, J = 5.0 Hz, 1H), 4.33 (ABX, J = 3.9 Hz, J = 11.9 Hz, 1H), 4.20-4.15 (m, 3H), 3.69 (d, J = 4.6 Hz, 2H), 2.45 (t, J = 2.3 Hz, 1H), 2.10, 2.07 (2s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.74, 170.40, 79.07, 75.12, 70.13, 67.95, 62.84, 58.65, 21.12, 20.85. $[\alpha]_d$ ($CHCl_3$, c = 1, 20°C) = + 7.5. Mass (TOF-MS-ESI$^+$): m/z: 237.07 (100%) $[M+Na]^+$. HRMS (TOF-MS-ESI$^+$, m/z): calculated for $C_{10}H_{14}O_5Na$: 237.0733; found: 237.0733.

Compound 16



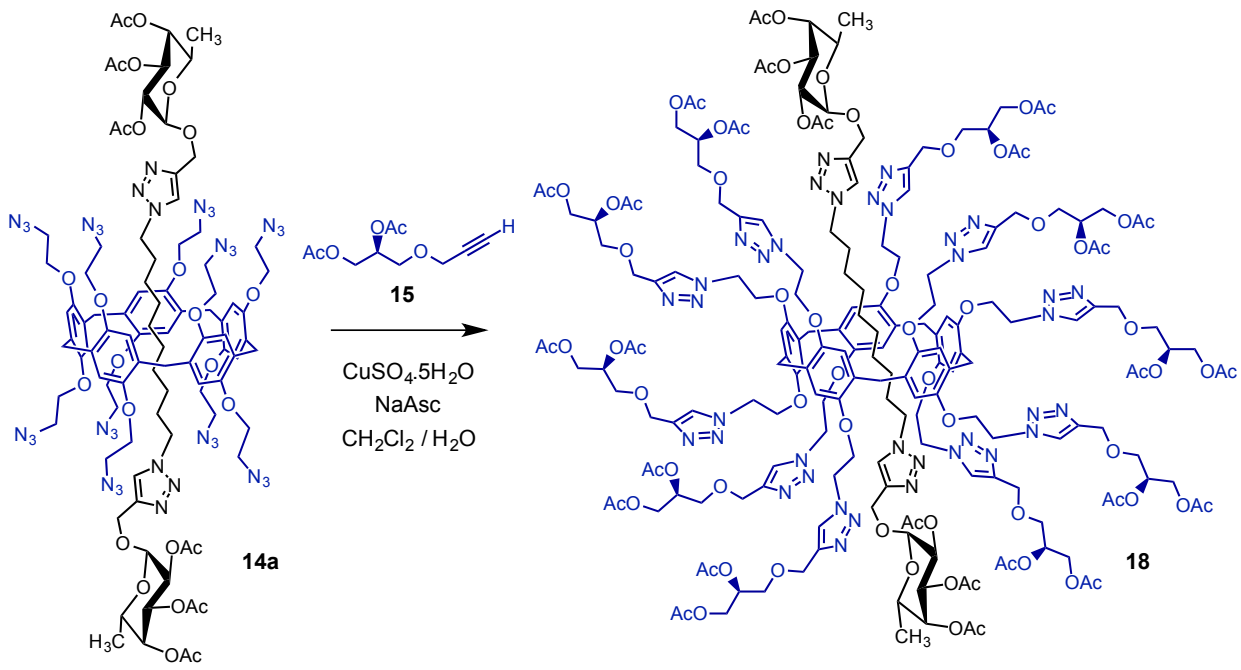
A mixture of **14a** (50 mg, 2.29 10^{-5} mol), **10** (106 mg, 2.74 10^{-4} mol), $CuSO_4 \bullet 5H_2O$ (0.3 mg, 2.29 10^{-6} mol) and sodium ascorbate (NaAsc, 1.3 mg, 6.87 10^{-6} mol) in CH_2Cl_2 (1 mL) / H_2O (0.5 mL) was stirred at room temperature during 4 h; then a saturated aqueous NH_4Cl solution (5 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (SiO_2, Cy to EtOAc/EtOH 8:2) gave **16** (118 mg, 85%) as a colorless solid. IR: 1745 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 and 7.76 (2s, 10H), 7.68 (s, 1H), 7.58 (s, 1H), 6.70 (s, 10H), 5.38 (bs, 10H), 5.31-5.10 (m), 5.04-4.93 (m), 4.79-4.62 (m), 4.30-4.09 (m), 3.98-3.93 (m, 10H), 3.78-3.61 (m, 4H), 3.40 (bs, 2H), 3.22 and 3.14 (2s, 10H), 2.16, 2.14, 2.13, 2.03, 2.03, 1.97, 1.93, 1.90 and 1.87 (9s, 138H), 1.13 (m, 6H), 0.59, 0.52, 0.30, 0.12, -0.11 and -0.27 (7bs, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.41, 170.26, 170.11, 169.53, 149.50, 149.40, 144.43, 143.44, 129.02, 123.33, 123.12, 115.88, 115.76, 100.42, 100.34, 70.81, 68.77, 67.42, 67.05, 64.81, 62.80, 62.68, 61.79, 61.12, 58.49, 50.33, 49.90, 30.18, 30.04, 29.30, 28.93, 28.86, 28.68, 25.73, 20.76, 20.72, 20.65, 15.95, 15.91. Mass (MALDI-TOF-LD+): m/z: 6094.2 (100%) $[M+K]^+$, 6045.4 (98%) $[M]^+$.

Compound 17



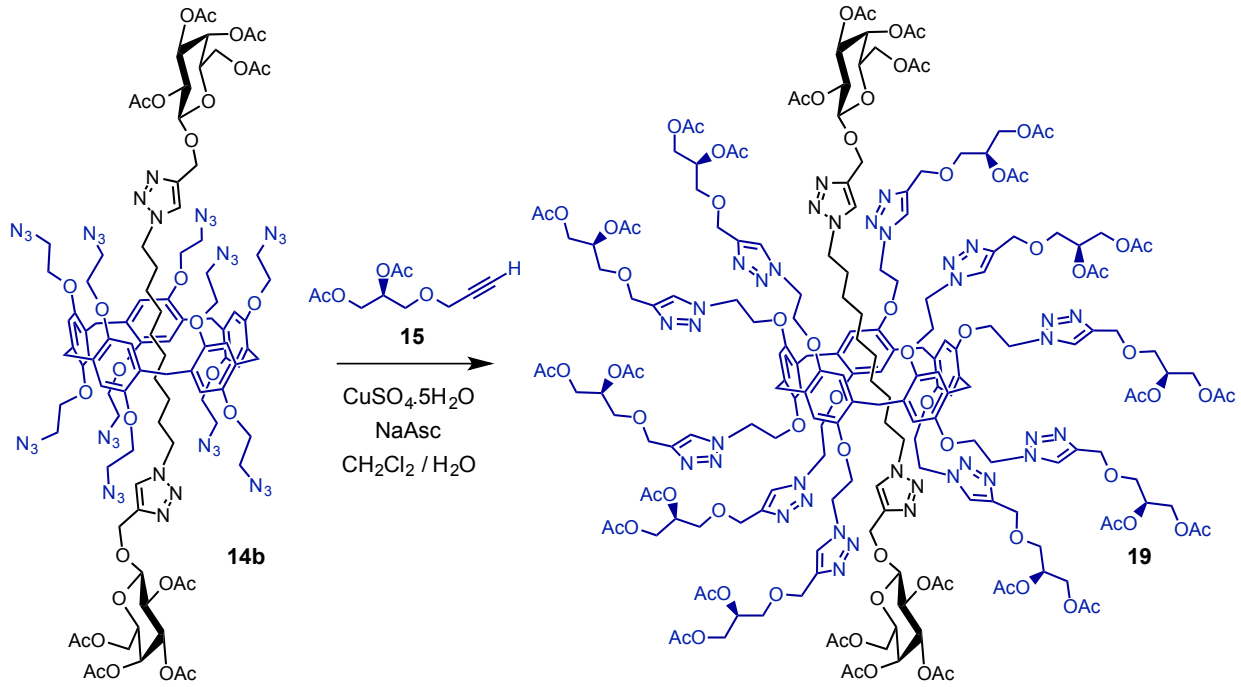
A mixture of **14b** (29 mg, 1.26 10^{-5} mol), **1** (50 mg, 1.51 10^{-4} mol), $CuSO_4 \bullet 5H_2O$ (0.2 mg, 1.26 10^{-6} mol) and sodium ascorbate (0.7 mg, 3.78 10^{-6} mol, 0.3 eq) in CH_2Cl_2 (0.5 mL) / H_2O (0.25 mL) was stirred at room temperature during 2 h; then a saturated aqueous NH_4Cl solution (5 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (SiO_2, Cy to EtOAc/EtOH 9:1) gave **17** (58 mg, 82%) as a colorless solid. IR: 1744 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 and 7.83 (2s, 10H), 7.43, 7.35 (2s, 2H), 6.64, 6.56 (2s, 10H), 5.41-5.08 (m), 4.86-4.62 (m), 4.26-3.97 (m), 3.26, 3.15 (2s, 10H), 2.20, 2.15, 2.10, 2.02, 2.01, 1.99, 1.97, 1.96 and 1.95 (9s, 114H), 1.06 and 0.95 (2d, J = 6.4 Hz, 30H), 0.50, 0.31, 0.06, -0.13 and -0.27 (5bs, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.40, 170.07, 170.03, 149.35, 144.54, 144.23, 128.99, 123.51, 115.67, 100.99, 95.91, 95.83, 71.14, 70.94, 68.91, 68.15, 68.02, 67.92, 67.23, 64.81, 64.74, 63.21, 62.80, 61.43, 61.27, 60.93, 50.32, 50.23, 49.67, 49.61, 30.35, 29.00, 28.81, 28.67, 20.84, 20.78, 20.75, 15.93, 15.83. Mass (MALDI-TOF-LD+): m/z: 5619.3 (100%) $[M+K]^+$, 5604.3 (75%) $[M+Na]^+$, 5581.3 (70%) $[M]^+$.

Compound 18



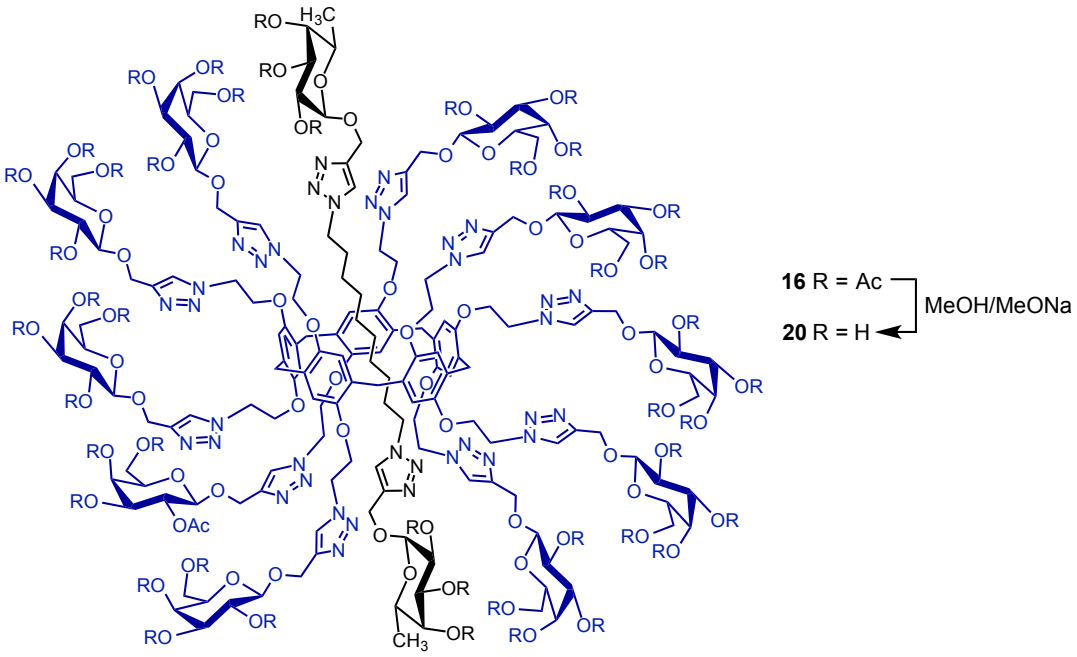
A mixture of **14a** (40 mg, 1.83 10^{-5} mol), **15** (59 mg, 2.74 10^{-4} mol), $CuSO_4 \bullet 5H_2O$ (0.3 mg, 1.83 10^{-6} mol) and sodium ascorbate (1.0 mg, 5.49 10^{-6} mol) in CH_2Cl_2 (0.8 mL) / H_2O (0.4 mL) was stirred at room temperature during 15 h; then a saturated aqueous solution of NH_4Cl (5 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (SiO_2, Cy to EtOAc/EtOH 9:1) gave **18** (51 mg, 65%) as a colorless oil. IR: 1736 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 and 7.83 (2s, 10H), 7.67 and 7.59 (2s, 2H), 6.60 and 6.58 (2s, 10H), 5.41-5.08 (m), 4.88-4.58 (m), 4.36-4.18 (m), 4.05, 4.02 (2d, J = 6.2 Hz, 10H), 3.61 (d, J = 5.3 Hz, 20H), 3.13 and 3.11 (2s, 10H), 2.14, 2.02, 2.01, 2.01, 1.99, 1.94, 1.93 and 1.88 (8s, 78H), 1.12 and 1.10 (2d, J = 6.4 Hz, 6H), 0.60 (bs, 2H), 0.50 (2bs, 2H), 0.17 (2bs, 2H), 0.02 (bs, 2H), -0.20 (2bs, 2H), -0.35 (2bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.70, 170.46, 170.37, 170.34, 170.15, 149.40, 144.86, 144.81, 143.43, 129.05, 128.99, 123.44, 123.13, 115.93, 115.77, 95.98, 95.77, 71.28, 71.18, 70.17, 70.12, 68.59, 68.33, 68.18, 67.87, 67.39, 67.32, 64.76, 62.82, 50.35, 49.95, 49.86, 30.08, 29.94, 29.53, 29.38, 28.88, 28.68, 25.81, 25.75, 21.06, 20.82, 20.76, 15.95. Mass (MALDI-TOF-LD+): m/z: 4346.8 (100%) $[M+Na]^+$, 4323.9 (30%) $[M]^+$.

Compound 19



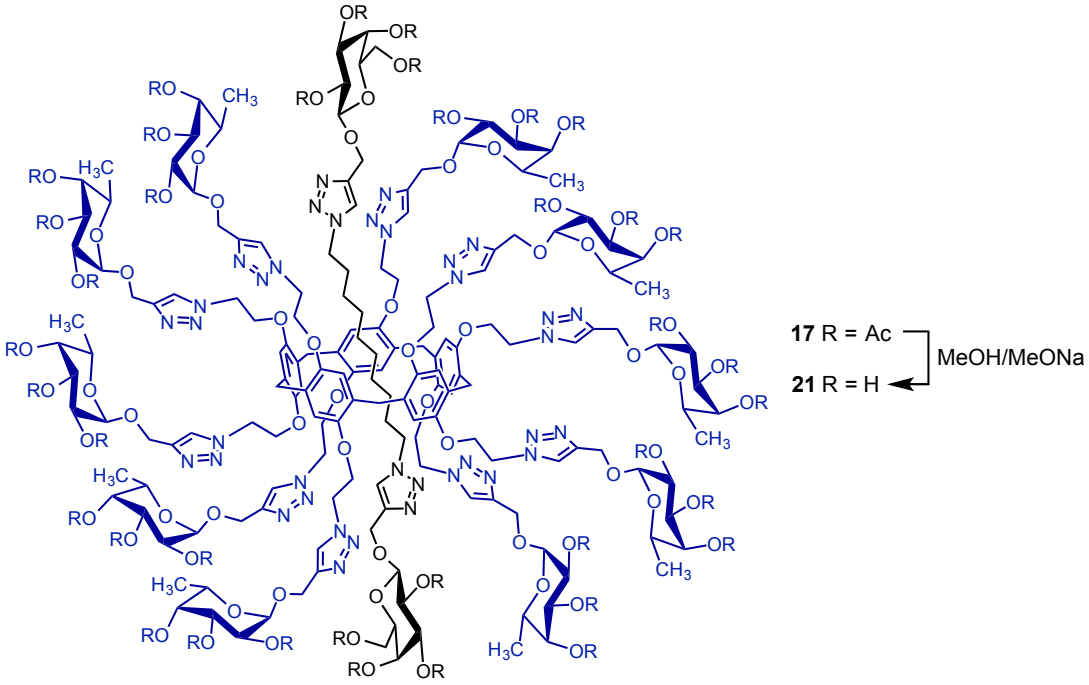
A mixture of **14b** (40 mg, 1.74 10^{-5} mol), **15** (56 mg, 2.61 10^{-4} mol), $CuSO_4 \bullet 5H_2O$ (0.3 mg, 1.74 10^{-6} mol) and sodium ascorbate (1.0 mg, 5.22 10^{-6} mol) in CH_2Cl_2 (0.8 mL) / H_2O (0.4 mL) was stirred at room temperature during 15 h, then a saturated aqueous solution of NH_4Cl (5 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (SiO_2, Cy to EtOAc/EtOH 9:1) gave **19** (61 mg, 79%) as a colorless oil. IR: 1738 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 and 7.83 (2s, 10H), 7.43 and 7.34 (2s, 2H), 6.58, 6.52 (2s, 10H), 5.39 (s, 2H), 5.20-5.05 (m), 4.83-4.58 (m), 4.24-3.98 (m), 3.61-3.59 (m, 20H), 3.09 (bs, 10H), 2.05, 2.01, 2.01, 2.00, 1.96, 1.95 and 1.94 (7s, 84H), 0.41 and 0.30 (2bs, 8H), 0.06 and -0.01 (2bs, 4H), -0.18 and -0.30 (2bs, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.73, 170.40, 170.35, 170.20, 170.08, 169.80, 149.33, 144.83, 144.74, 143.06, 129.03, 128.97, 123.60, 123.46, 123.16, 122.97, 115.81, 100.99, 100.69, 70.85, 70.16, 70.11, 68.90, 68.59, 67.27, 67.11, 64.67, 62.82, 61.07, 61.00, 50.38, 50.32, 49.70, 30.22, 28.88, 25.99, 25.75, 21.05, 20.82, 20.73, 20.63, 20.48.

Compound 20



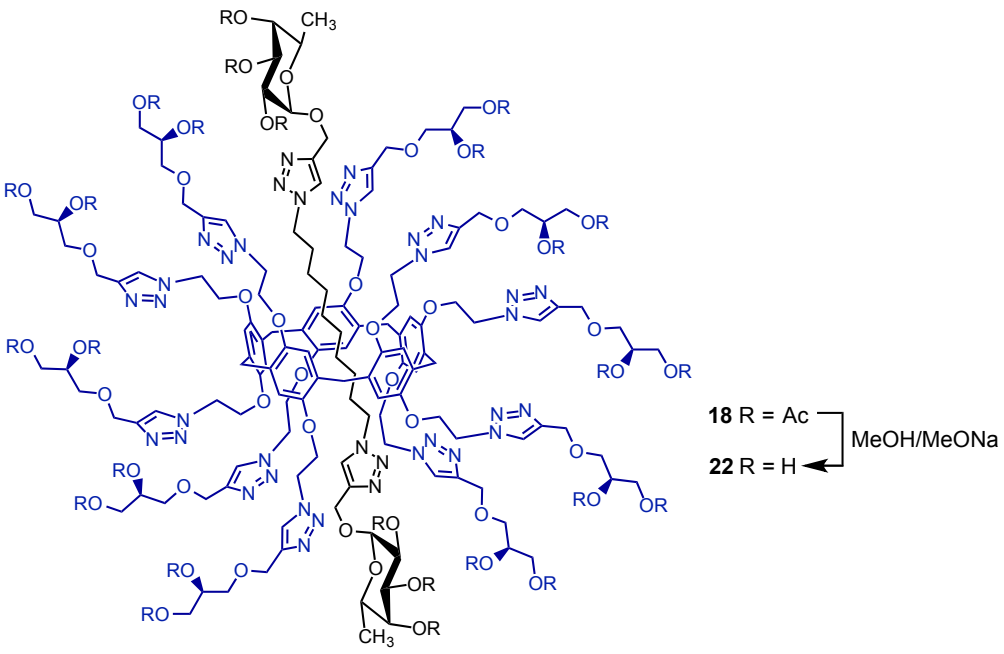
To a solution of **16** (40 mg, 6.6 10^{-6} mol) in MeOH (0.5 mL) was added sodium methoxide (4 mg, 6.6 10^{-5} mol) at 0°C. The solution was then stirred during two hours at room temperature and filtered over a short column of Dowex™ 50WX8-200 (H^+ resin form). The resin was washed with water (5 mL) and solvents were evaporated under reduced pressure to afford **20** (24 mg, 86%) as colorless glassy product. ^{1}H NMR (400 MHz, D_2O) δ = 8.27 (s, 10H), 7.88 and 7.85 (2s, 2H), 6.53 and 6.42 (2bs, 10H), 5.06-4.69 (m), 4.27-4.18 (m), 3.99-3.93 (m, 2H), 3.80-3.60 (m), 3.52-3.44 (m), 3.34-3.23 (m), 3.04 (bs), 1.10 (dd, 6.0 Hz, J = 6.2 Hz, 6H), 0.57 (bs, 4H), -0.06 and -0.10 (2bs, 4H), -0.44 and -0.48 (2bs, 8H). ^{13}C NMR (100 MHz, D_2O) δ =149.60, 149.44, 144.00, 143.72, 129.26, 128.90, 125.54, 125.33, 116.02, 115.68, 101.18, 101.09, 98.83, 98.62, 75.24, 75.10, 72.67, 71.73, 71.69, 71.60, 70.63, 69.62, 68.64, 68.56, 68.01, 67.61, 67.23, 66.76, 61.28, 61.07, 60.96, 60.44, 50.49, 50.13, 29.63, 29.21, 28.39, 25.43, 15.33. Mass (MALDI-TOF-LD+): m/z: 4134.8 $[M]^+$.

Compound 21



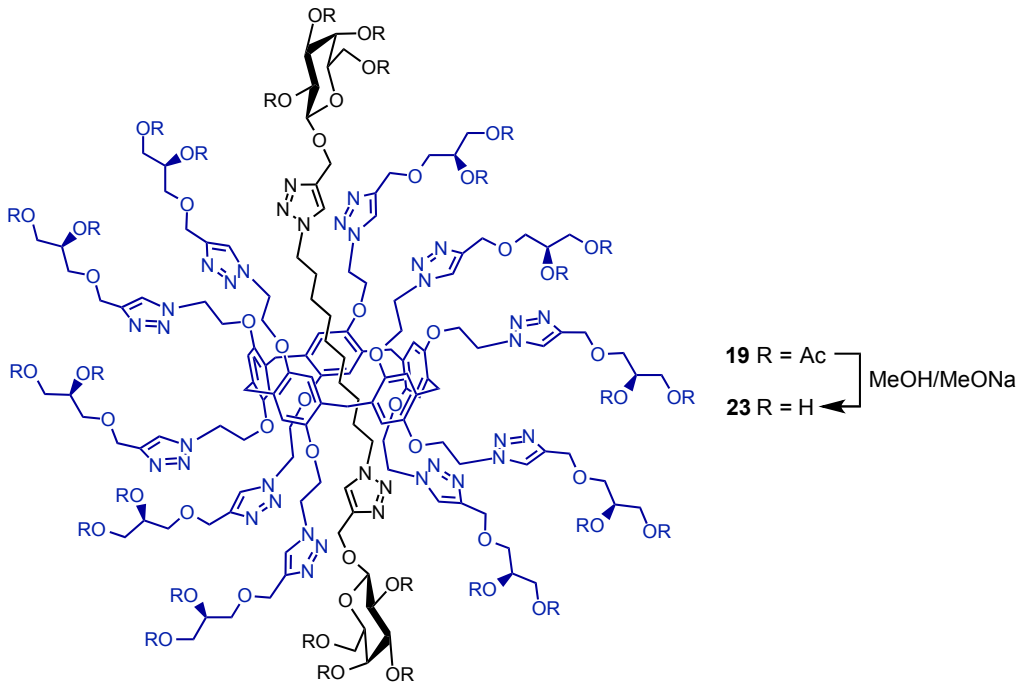
To a solution of **17** (20 mg, 3.58 10^{-6} mol) in MeOH (0.5 mL) was added sodium methoxide (1.9 mg, 3.58 10^{-5} mol) at room temperature. The solution was stirred during 2 h at room temperature then filtered over a short column of Dowex™ 50WX8-200 (H^+ resin form). The resin was washed with water (5 mL) and solvents were evaporated under reduced pressure to afford **21** (13 mg, 91%) as colorless foam. ^{1}H NMR (400 MHz, D_2O) δ = 8.35 and 8.27 (2s, 10H), 7.65 and 7.56 (2s, 2H), 6.45 and 6.35 (2s, 10H), 4.98-4.50 (m), 4.15-2.98 (m), 0.88, 0.82 (2d, J = 6.4 Hz, 30H), 0.38, 0.25, 0.00, -0.11, -0.23 and -0.30 (6bs, 16H). ^{13}C NMR (100 MHz, D_2O) δ = 149.16, 144.86, 144.66, 128.68, 125.14, 115.23, 102.35, 98.80, 98.46, 75.29, 72.92, 71.74, 71.64, 70.90, 70.74, 69.51, 68.64, 68.11, 68.01, 67.04, 66.69, 61.08, 60.77, 50.36, 15.27. Mass (TOF-MS-ESI$^+$): m/z: 1350.9211 $[M+3Na]^{3+}$.

Compound 22



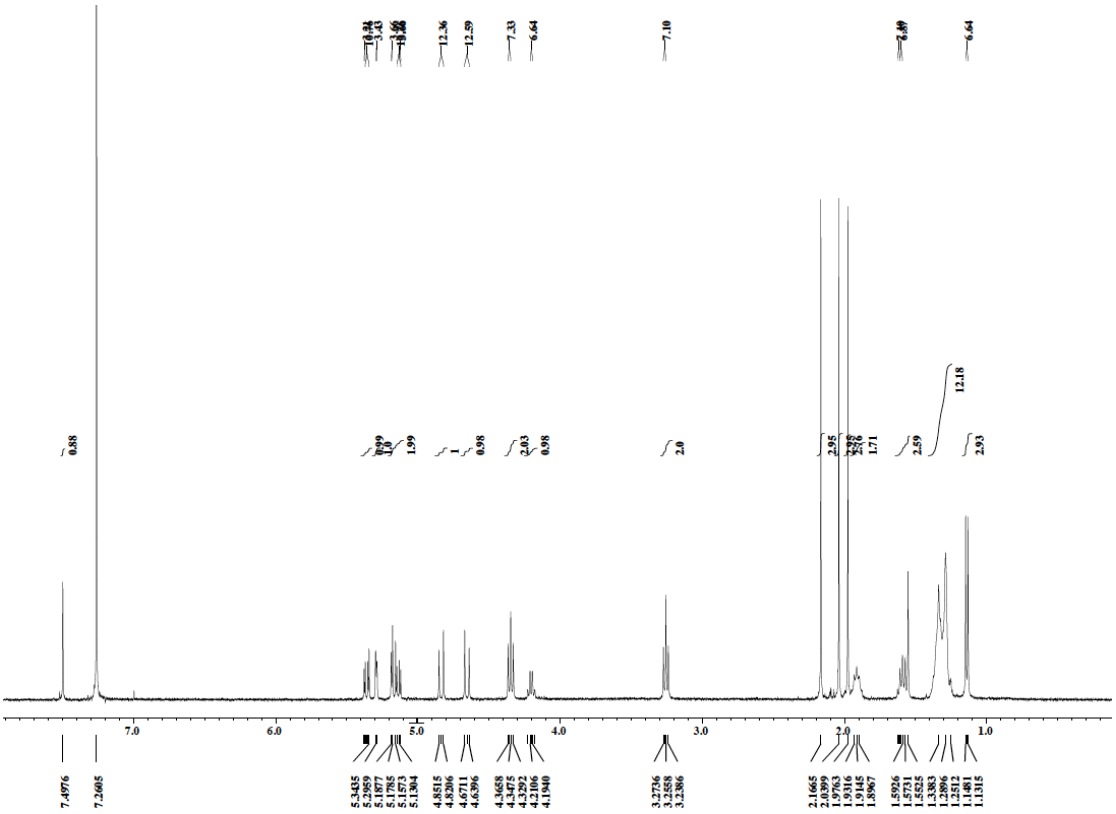
To a solution of **18** (30 mg, 6.93 10^{-6} mol) in MeOH (0.5 mL) was added sodium methoxide (4 mg, 6.93 10^{-5} mol) at room temperature. The solution was stirred during 2 h at room temperature then filtered over a short column of Dowex™ 50WX8-200 (H^+ resin form). The resin was washed with water (5 mL) and solvents were evaporated under reduced pressure to afford **22** (20 mg, 89%) as a colorless foam. ^{1}H NMR (400 MHz, D_2O) δ = 8.19 (s, 10H), 7.84 and 7.83 (2s, 2H), 6.44 and 6.43 (2s, 10H), 5.05 (bs, 2H), 4.75-4.56 (m,), 4.17 (bs, 20H), 4.00-3.90 (m, 2H), 3.81-3.22 (m), 2.89 and 2.85 (2bs, 10H), 1.10 and 1.09 (2d, J = 6.4 Hz, 6H), 0.83 (bs, 2H), 0.53 (bs, 4H), -0.06 and -0.10 (2bs, 4H), -0.46 (bs, 6H). ^{13}C NMR (100 MHz, D_2O) δ = 149.43, 144.48, 144.39, 143.83, 129.02, 128.96, 125.00, 124.90, 124.02, 116.10, 115.91, 98.87, 98.62, 71.79, 71.72, 70.89, 70.81, 70.36, 70.31, 69.66, 68.01, 67.50, 66.79, 63.33, 62.48, 50.40, 50.14, 29.54, 29.18, 28.36, 28.11, 25.38, 15.35. Mass (TOF-MS-ESI$^-$): m/z: 1075.7 $[M-H]^{3-}$.

Compound 23

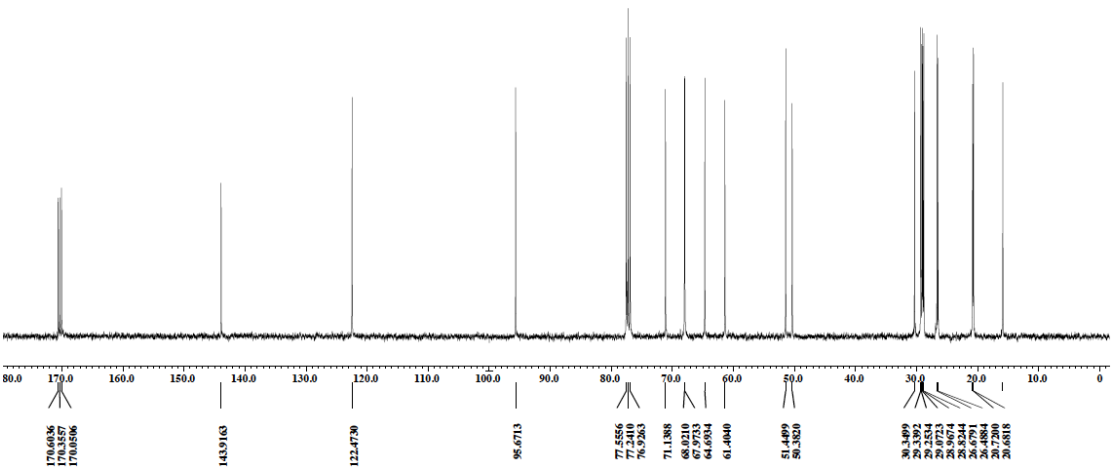


To a solution of **19** (31 mg, 6.98 10^{-6} mol) in MeOH (0.5 mL) was added sodium methoxide (4 mg, 6.98 10^{-5} mol) at room temperature. The solution was stirred during 2 h at room temperature then filtered over a short column of Dowex™ 50WX8-200 (H^+ resin form). The resin was washed with water (10 mL) and solvents were evaporated under reduced pressure to afford **23** (20 mg, 88%) as colorless foam. ^{1}H NMR (400 MHz, D_2O) δ = 8.19 and 8.18 (2s, 10H), 7.67 (s, 2H), 6.46 and 6.44 (2s, 10H), 5.06 (dd, J = 9.9 Hz, J = 12.1 Hz, 2H), 4.83 (bs), 4.65-4.56 (m, 2H), 4.17 (bs, 20H), 3.90 (bs, 2H), 3.81-3.50 (m), 3.44-3.24 (m), 2.90 and 2.87 (2bs, 10H), 0.39 (bs, 4H), 0.17 (bs, 4H), -0.18 (bs, 4H), -0.35 (bs, 4H). ^{13}C NMR (100 MHz, D_2O) δ =149.37, 144.35, 143.44, 128.90, 125.03, 124.92, 123.95, 115.38, 102.38, 75.27, 72.91, 70.87, 70.80, 70.30, 68.62, 67.44, 63.31, 62.47, 61.78, 61.07, 50.39, 49.89, 29.72, 28.73, 28.50, 28.03, 25.50.

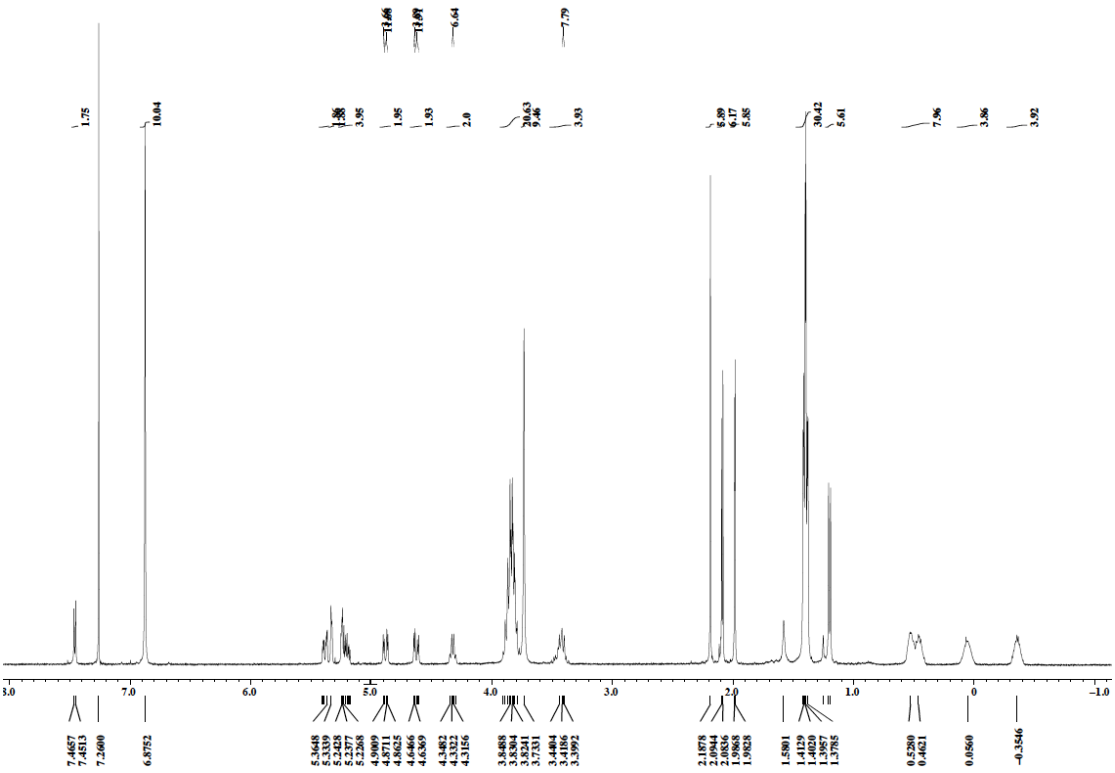
^{1}H NMR spectrum of compound **3** ($CDCl_3$, 400 MHz)



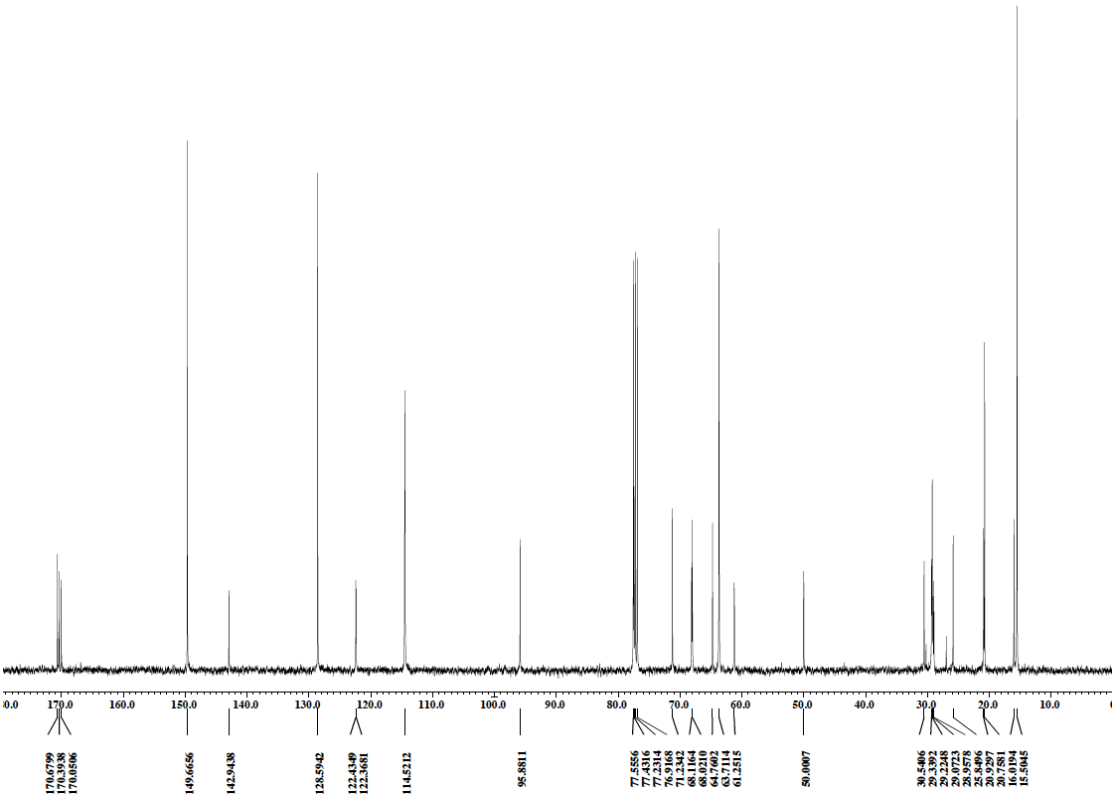
^{13}C NMR spectrum of compound **3** ($CDCl_3$, 100 MHz)



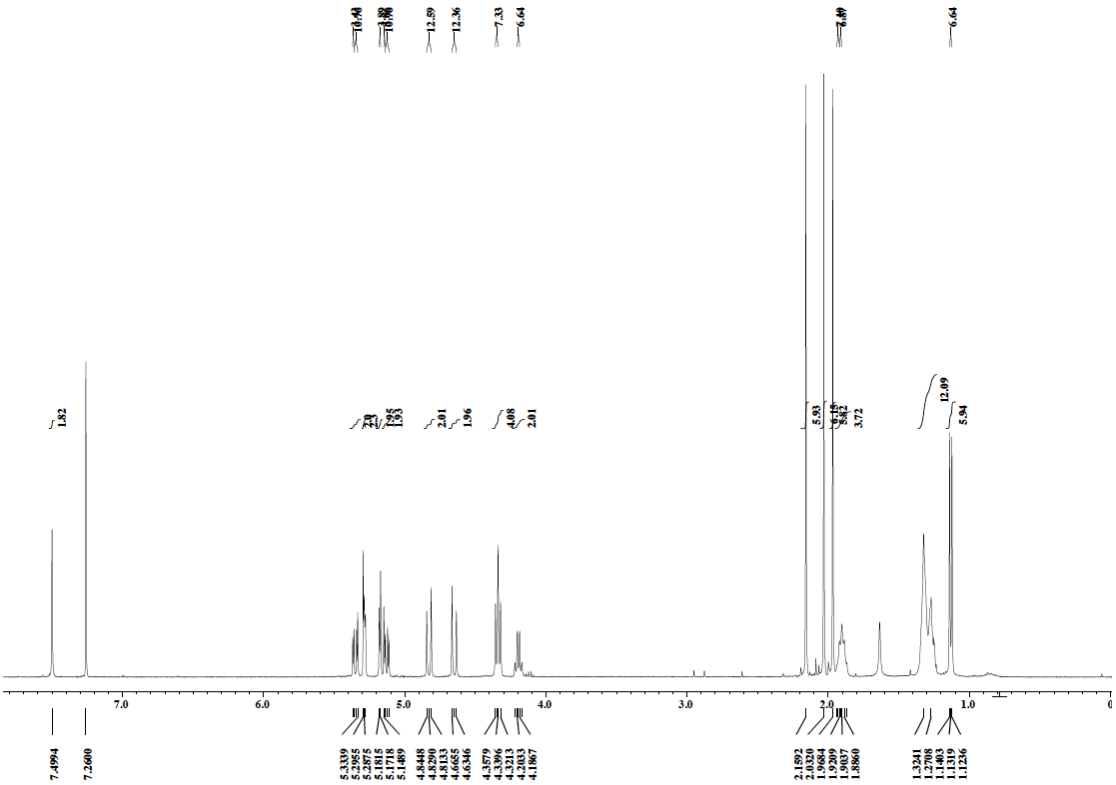
^{1}H NMR spectrum of compound **5** ($CDCl_3$, 400 MHz)



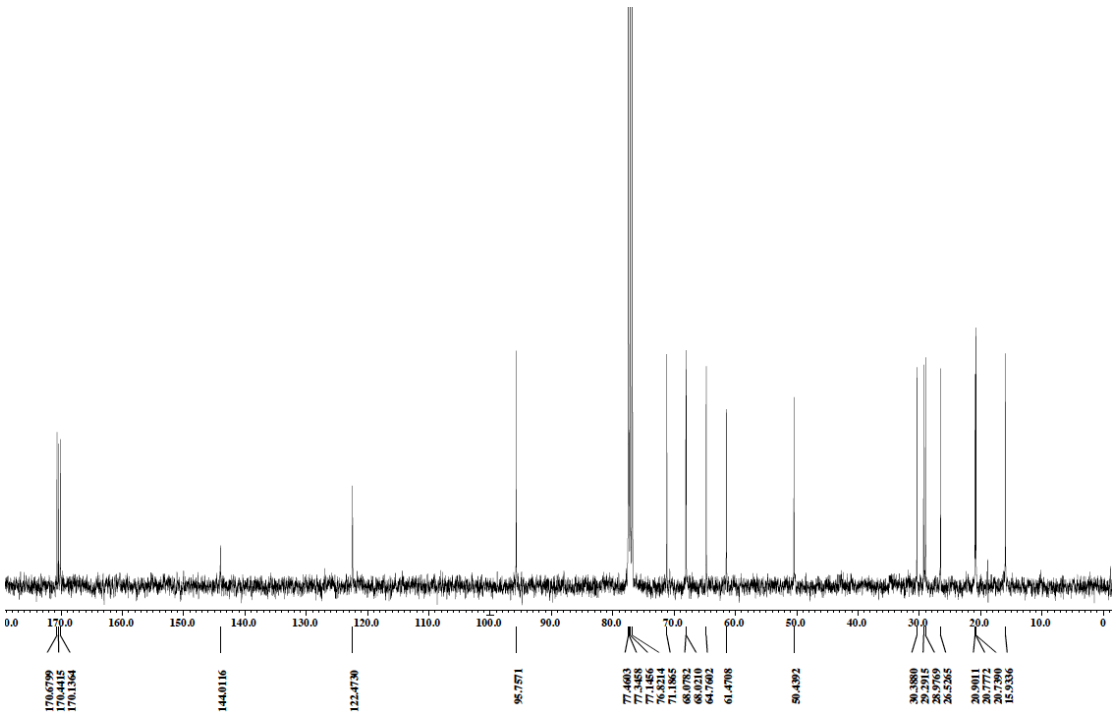
^{13}C NMR spectrum of compound **5** ($CDCl_3$, 100 MHz)



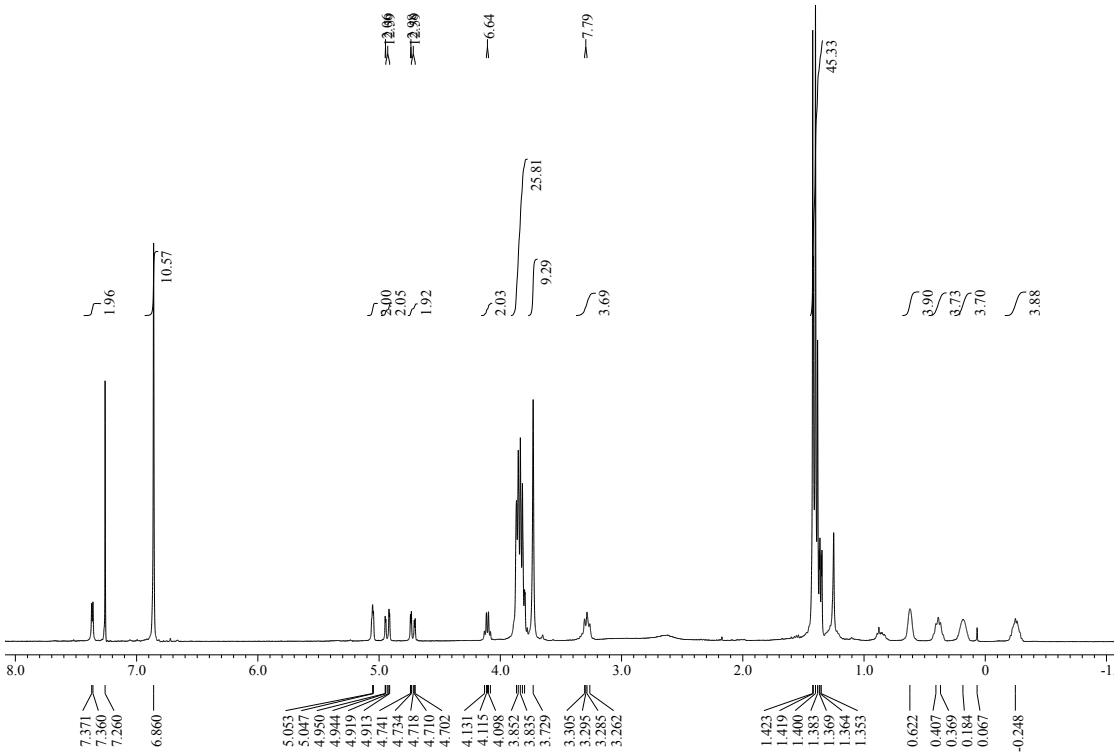
^{1}H NMR spectrum of compound **6** ($CDCl_3$, 400 MHz)



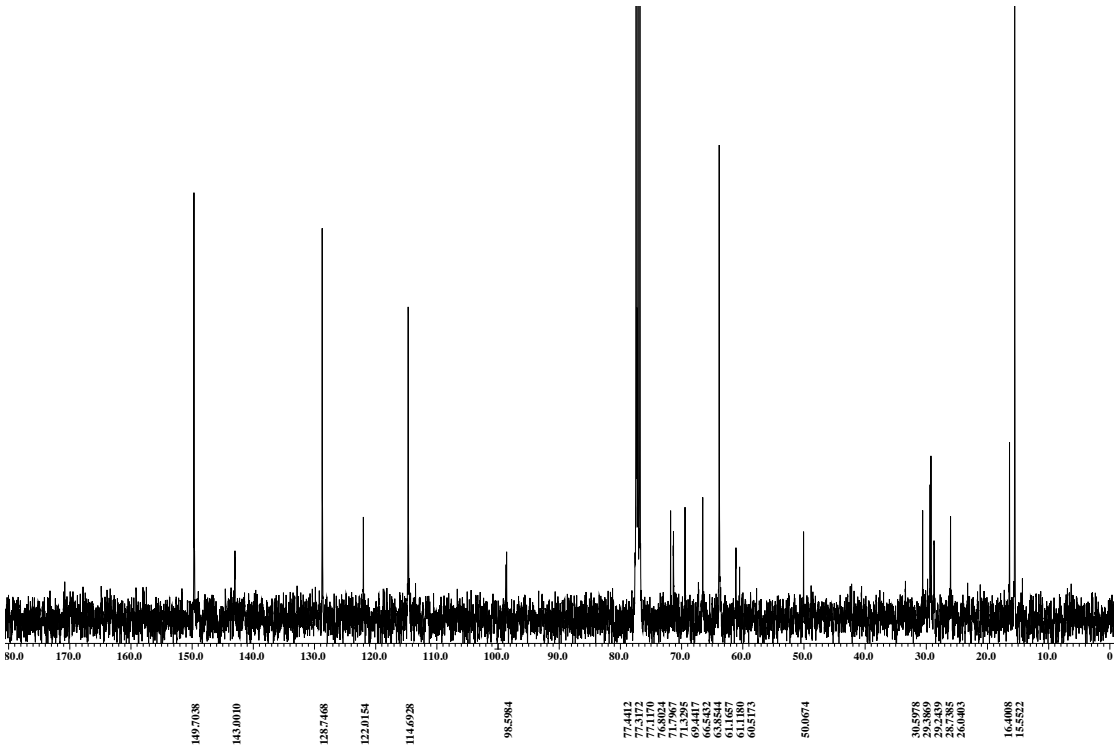
^{13}C NMR spectrum of compound **6** ($CDCl_3$, 100 MHz)



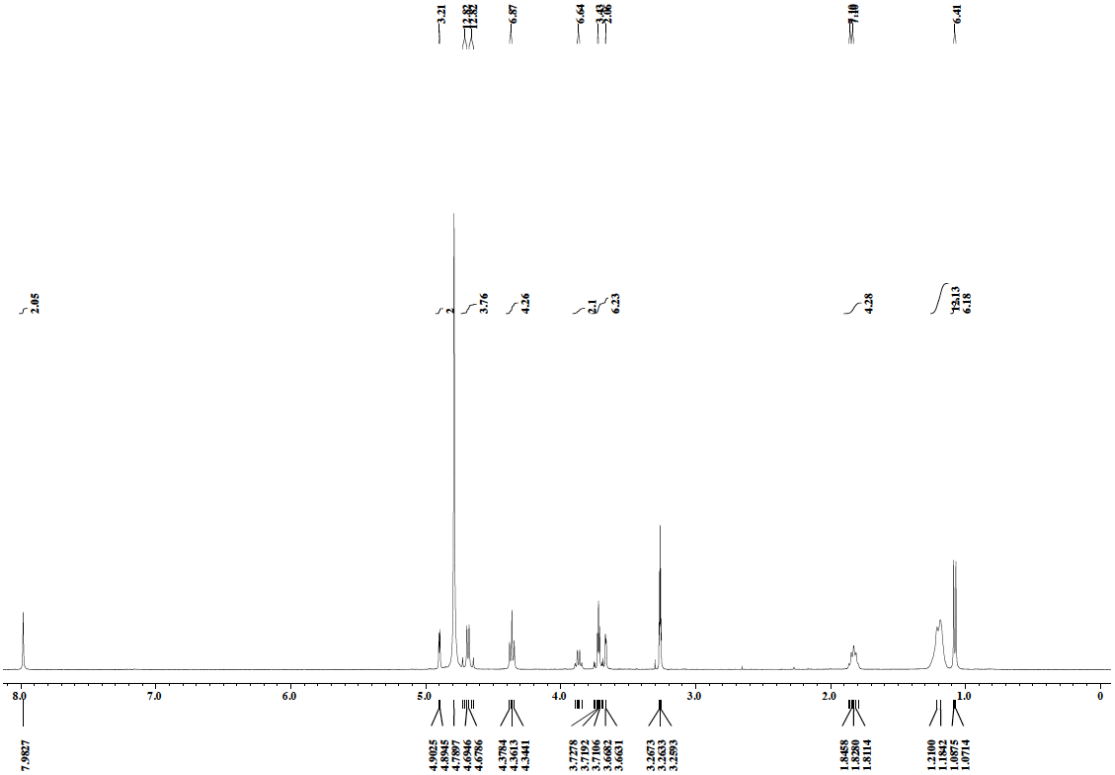
^{1}H NMR spectrum of compound **7** ($CDCl_3$, 400 MHz)



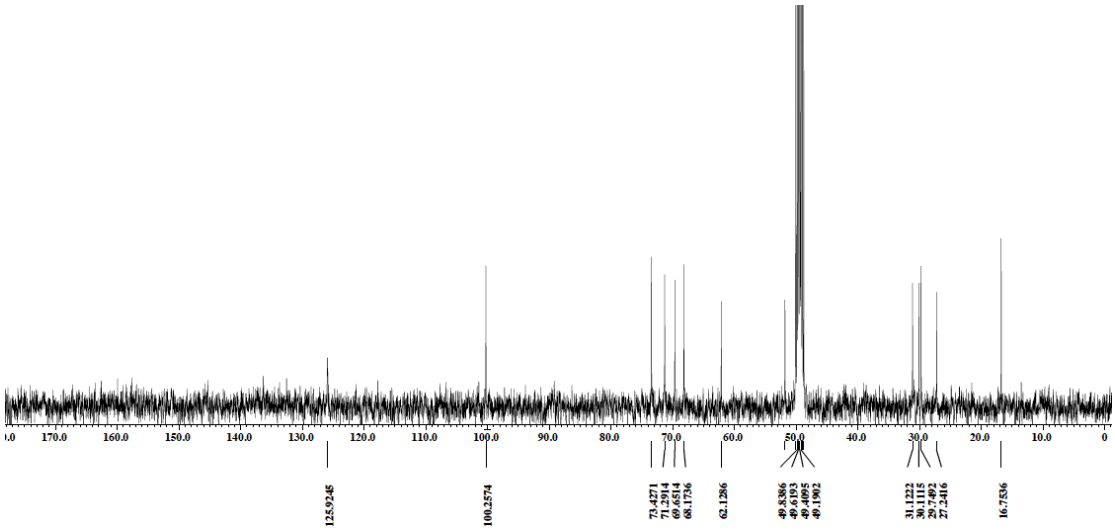
^{13}C NMR spectrum of compound **7** ($CDCl_3$, 100 MHz)



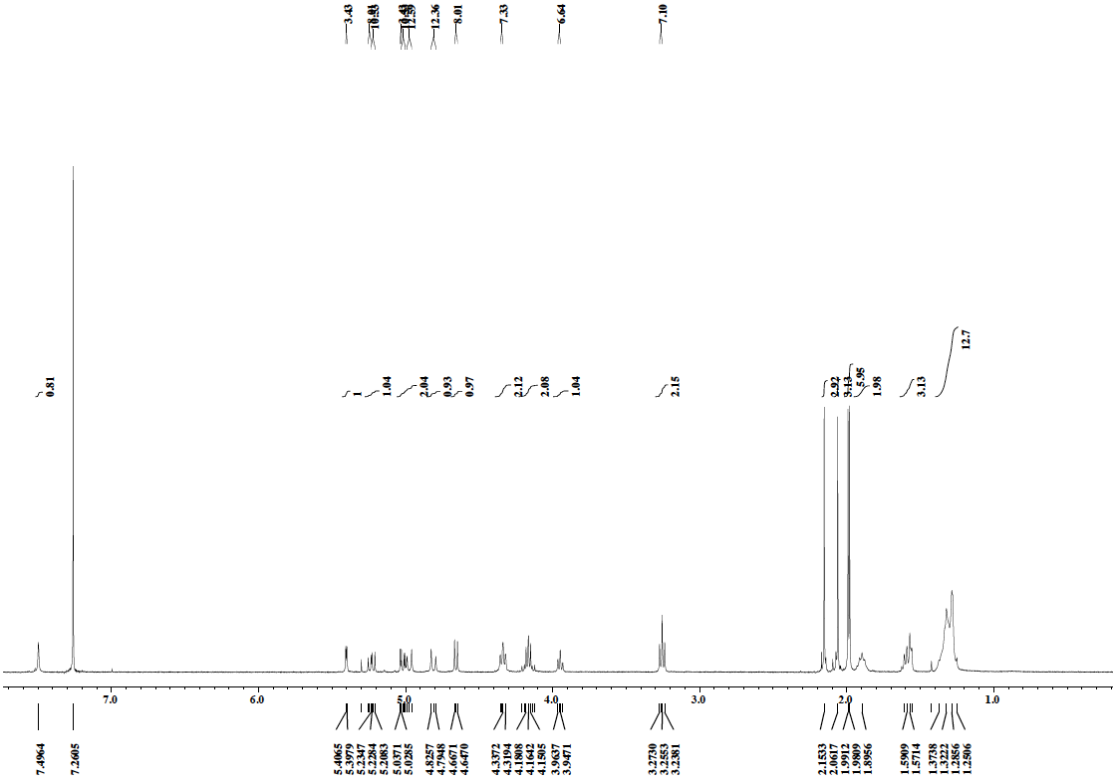
^{1}H NMR spectrum of compound **8** (D_2O/CD_3OD 1:1, 400 MHz)



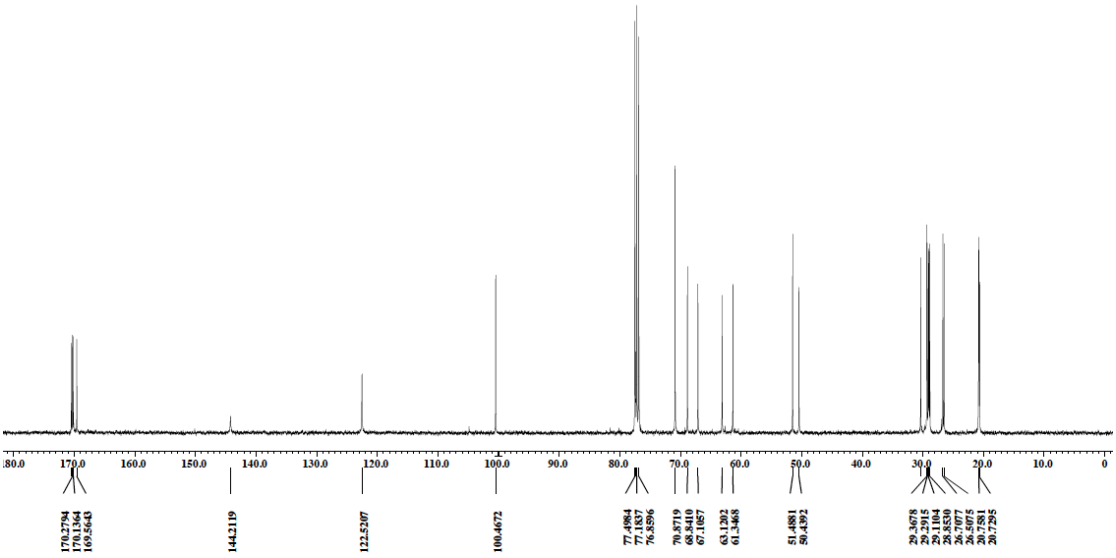
^{13}C NMR spectrum of compound **8** (D_2O/CD_3OD 1:1, 100 MHz)



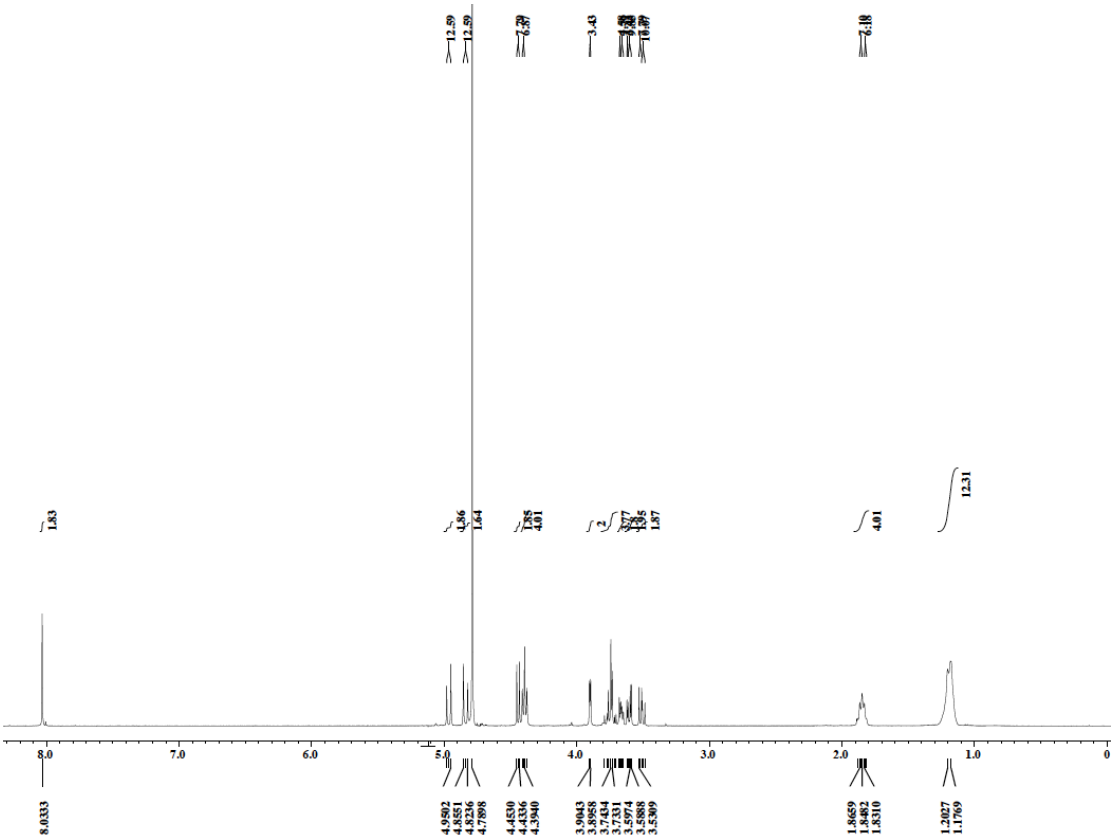
^{1}H NMR spectrum of compound **11** ($CDCl_3$, 400 MHz)



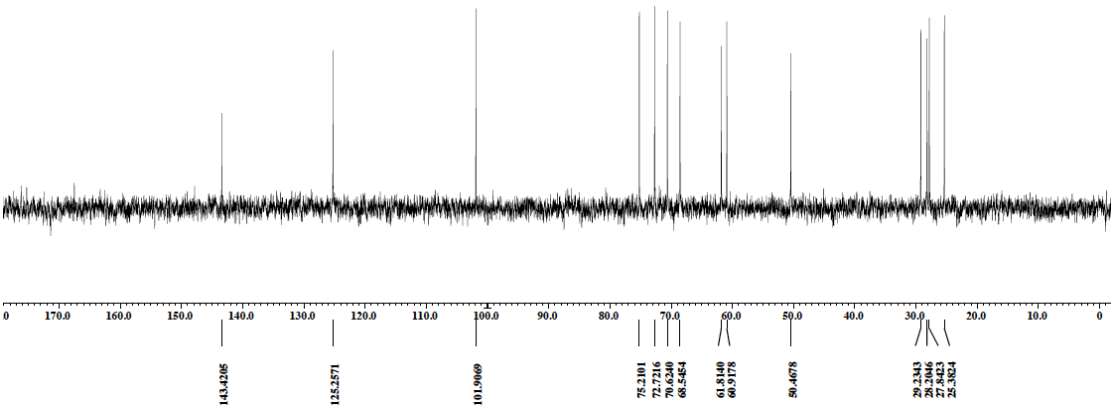
^{13}C NMR spectrum of compound **11** ($CDCl_3$, 100 MHz)



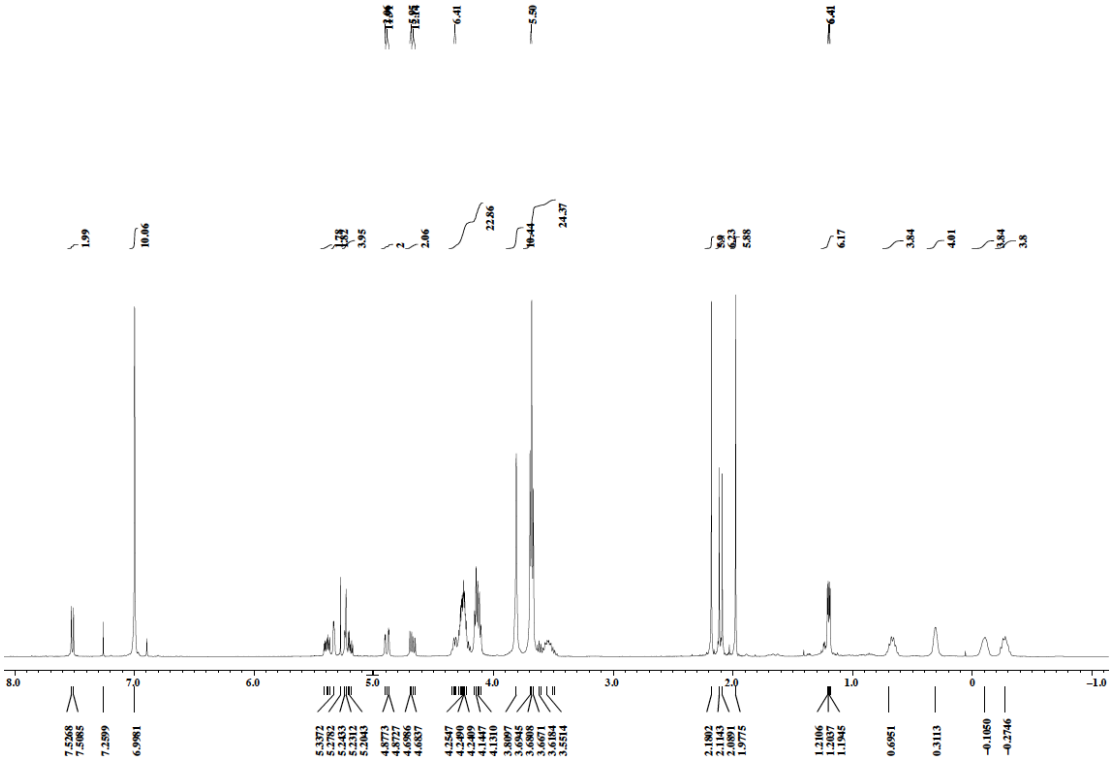
^{1}H NMR spectrum of compound **12** ($CDCl_3$, 400 MHz)



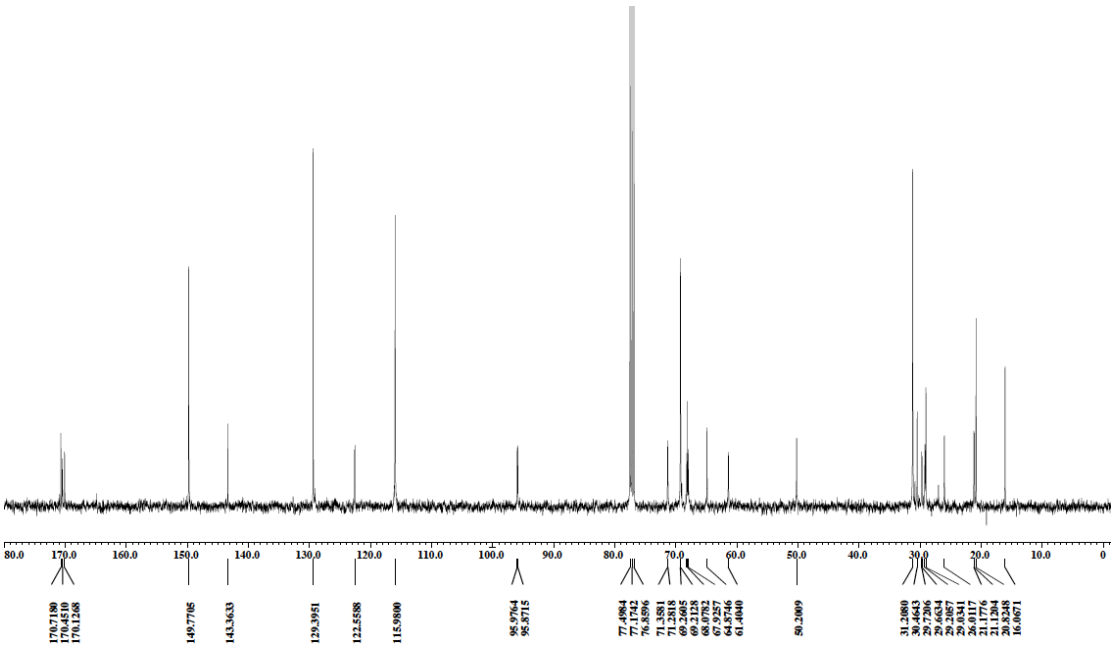
^{13}C NMR spectrum of compound **12** ($CDCl_3$, 100 MHz)



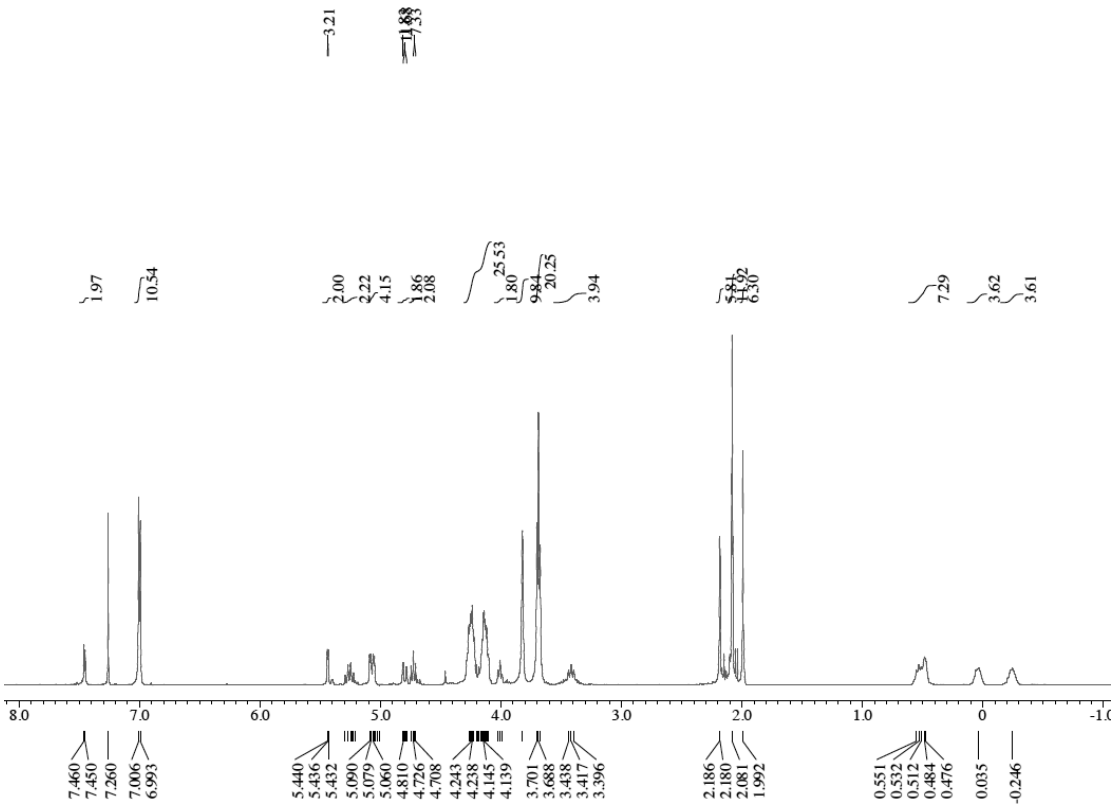
^{1}H NMR spectrum of compound **13a** ($CDCl_3$, 400 MHz)



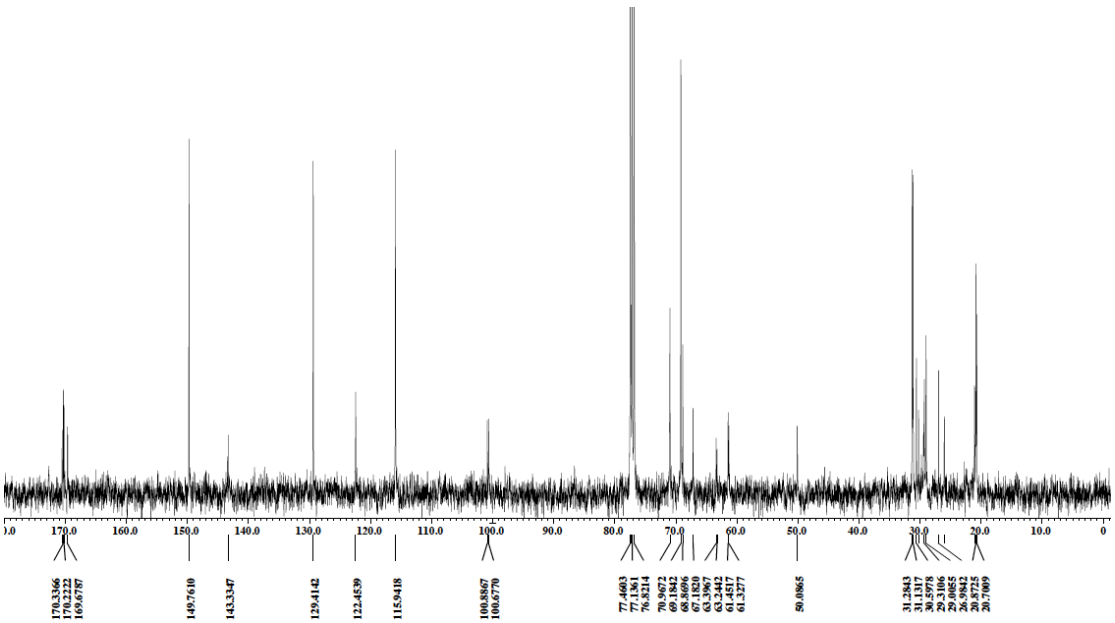
^{13}C NMR spectrum of compound **13a** ($CDCl_3$, 100 MHz)



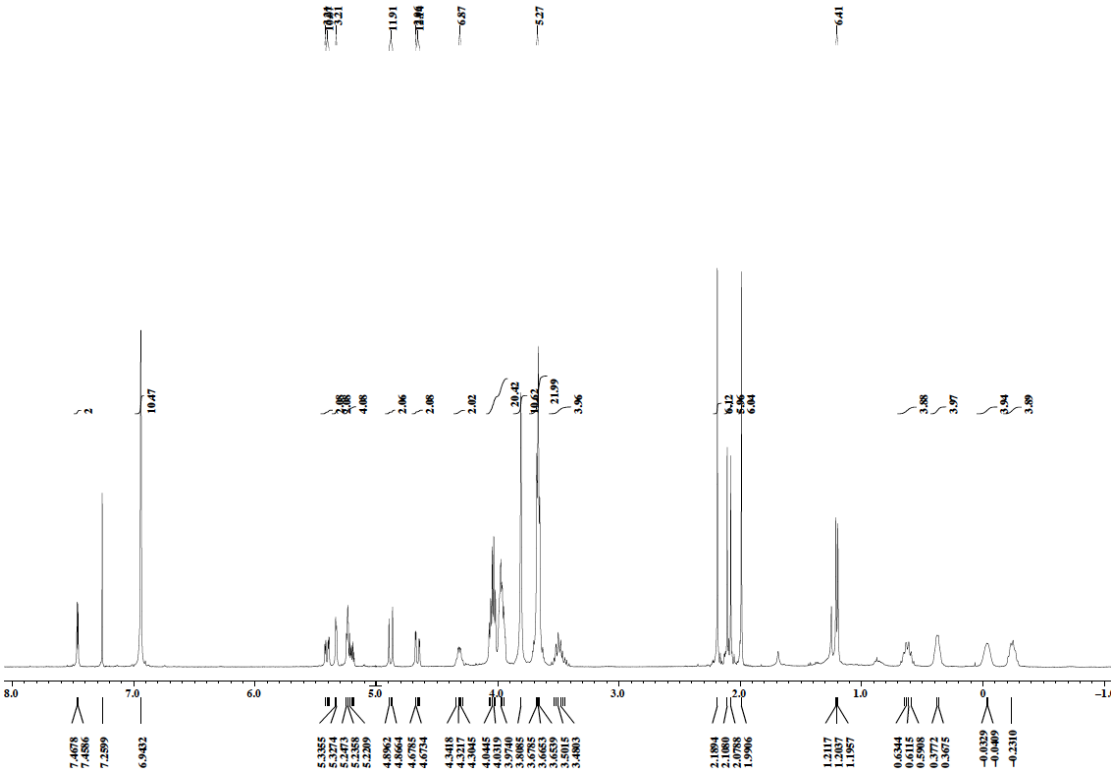
^{1}H NMR spectrum of compound **13b** ($CDCl_3$, 400 MHz)



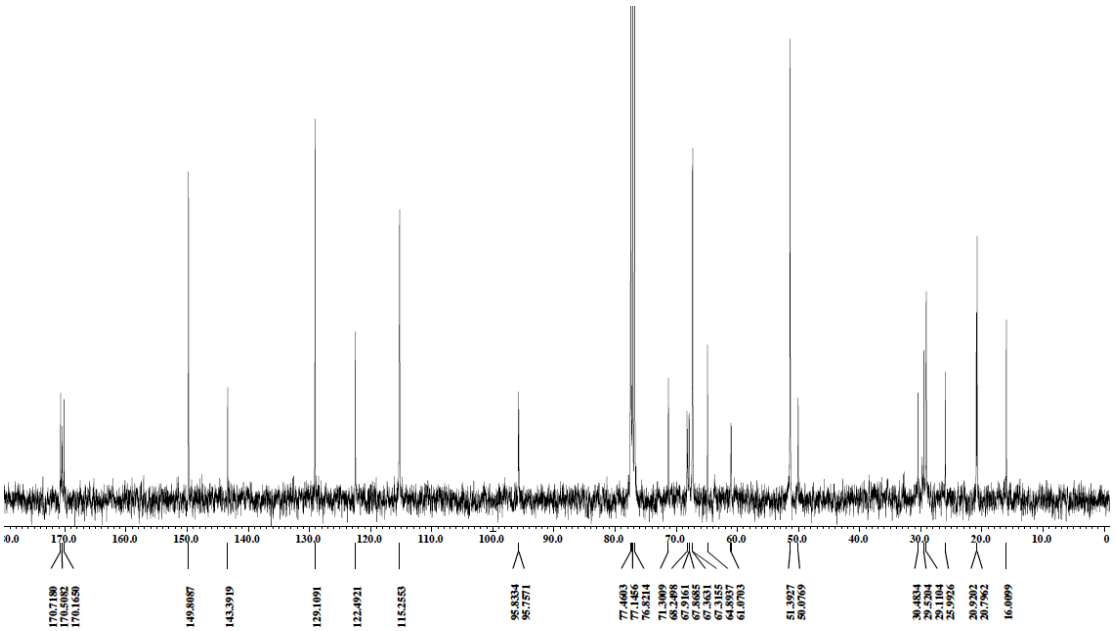
^{13}C NMR spectrum of compound **13b** ($CDCl_3$, 100 MHz)



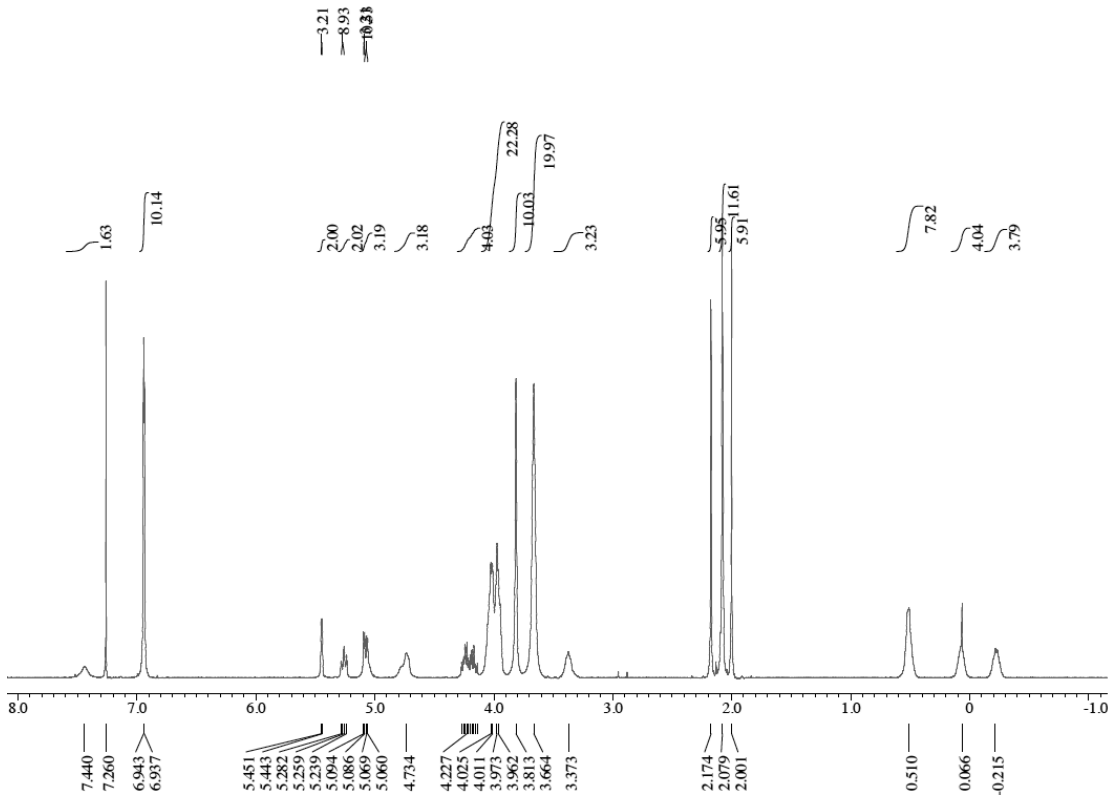
^{1}H NMR spectrum of compound **14a** ($CDCl_3$, 400 MHz)



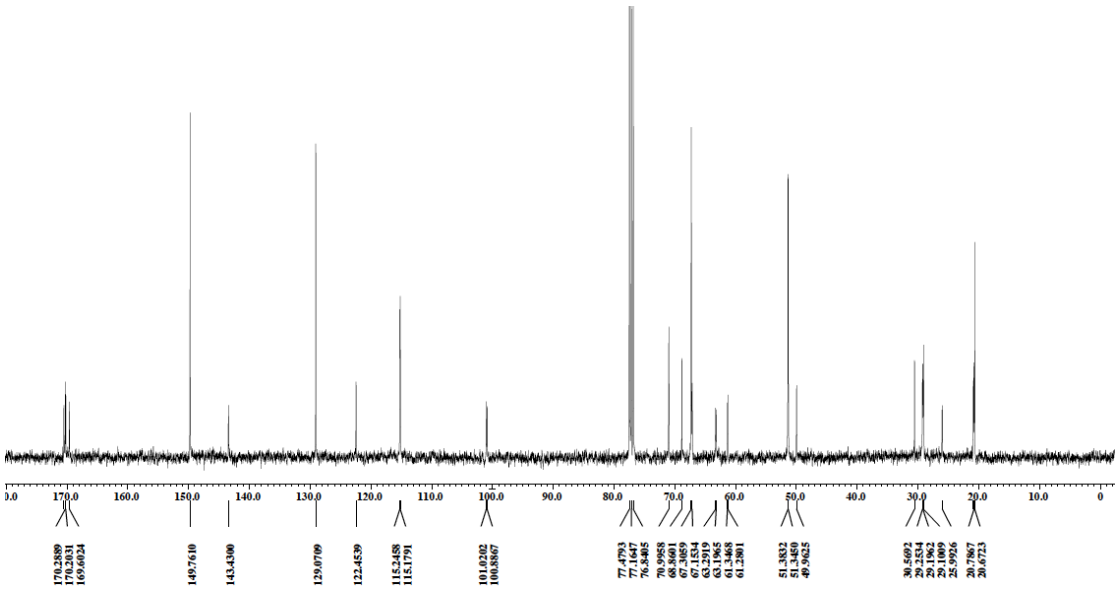
^{13}C NMR spectrum of compound **14a** ($CDCl_3$, 100 MHz)



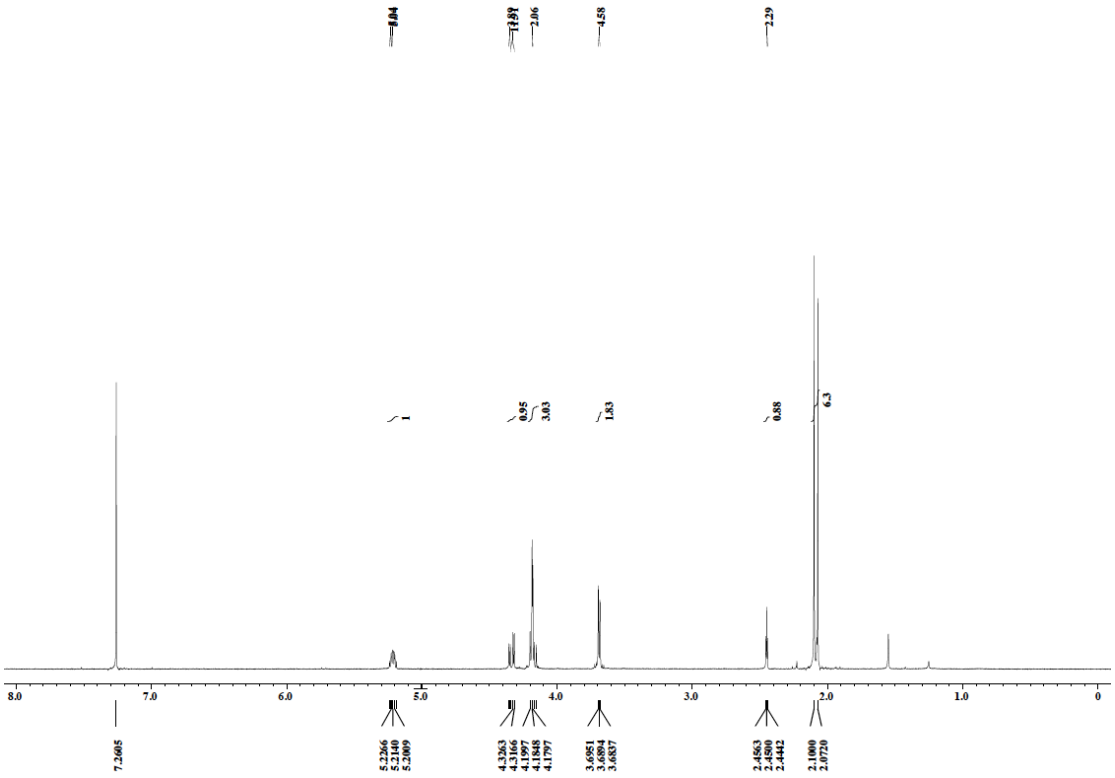
^{1}H NMR spectrum of compound **14b** ($CDCl_3$, 400 MHz)



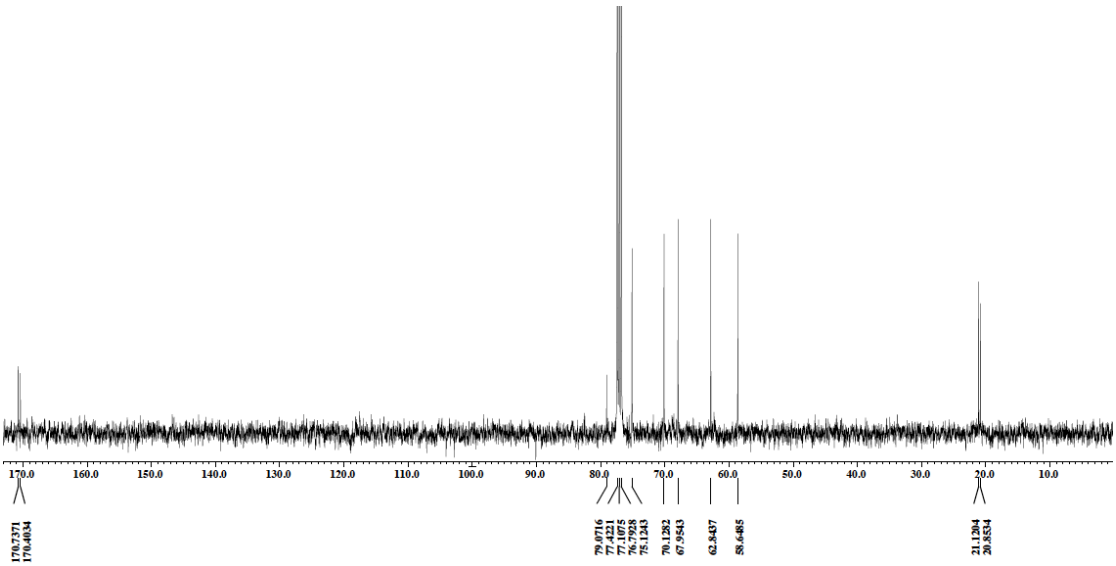
^{13}C NMR spectrum of compound **14b** ($CDCl_3$, 100 MHz)



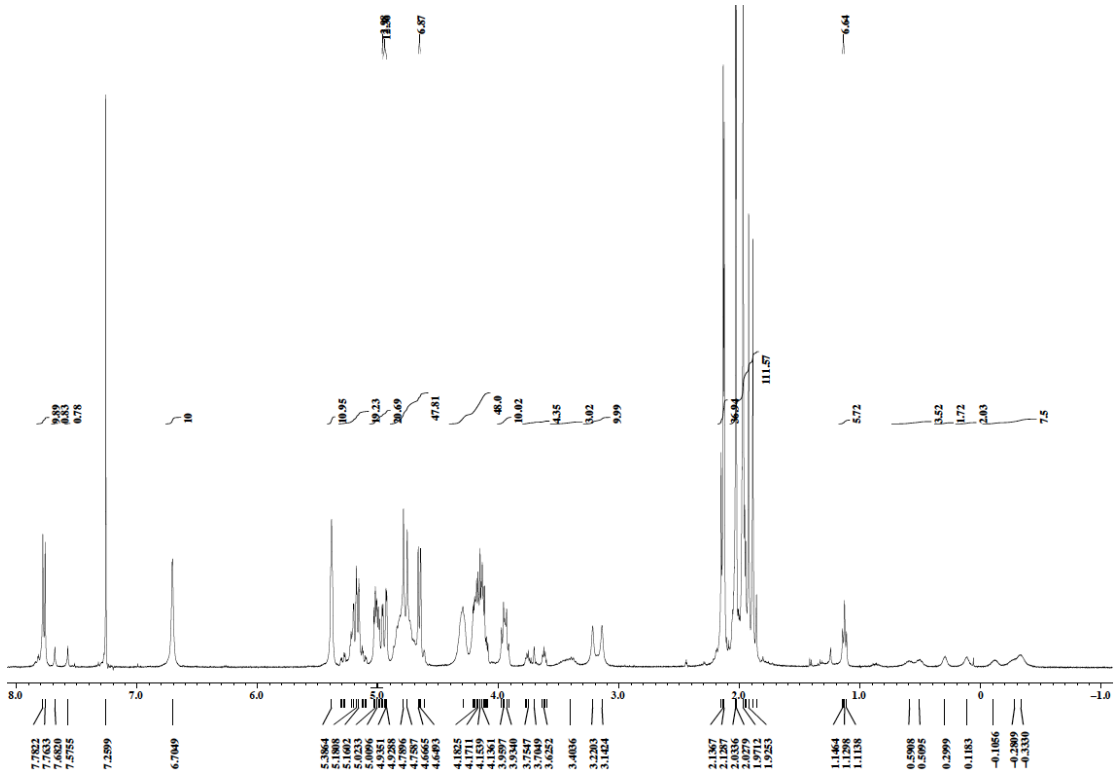
^{1}H NMR spectrum of compound **15** ($CDCl_3$, 400 MHz)



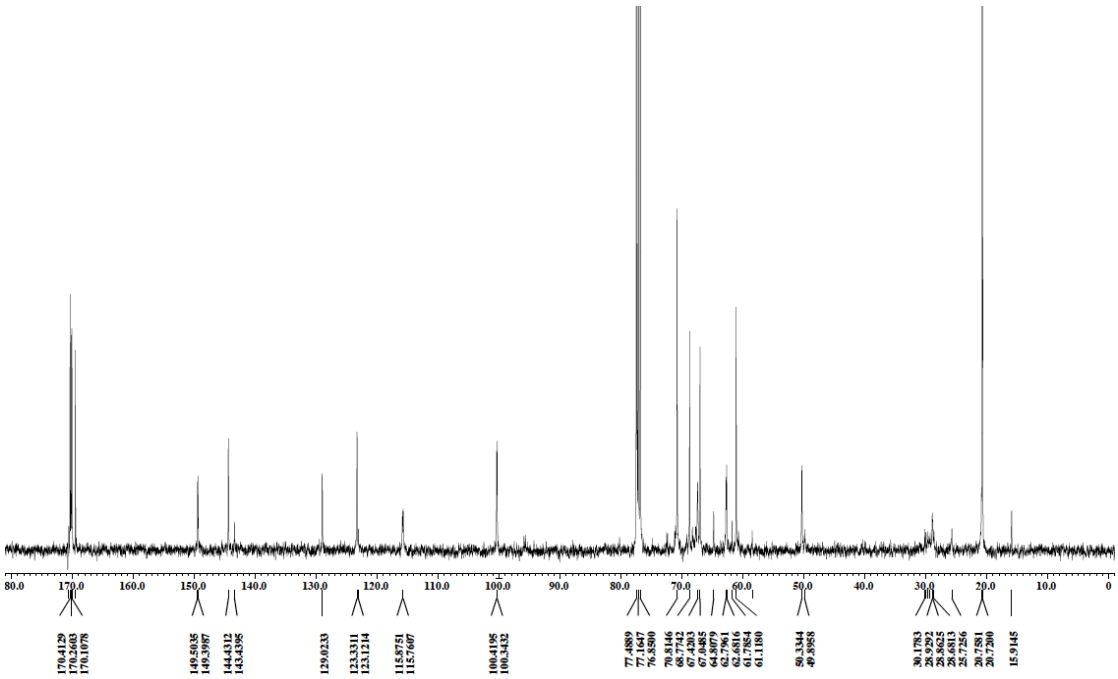
^{13}C NMR spectrum of compound **15** ($CDCl_3$, 100 MHz)



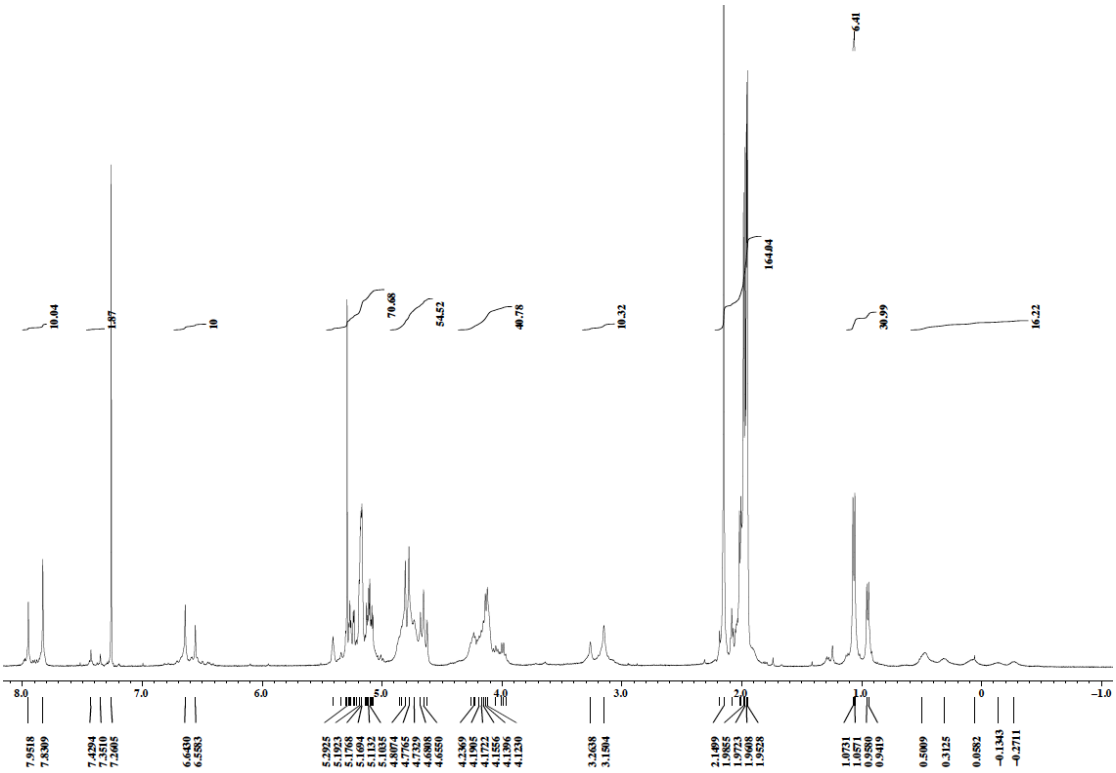
^{1}H NMR spectrum of compound **16** ($CDCl_3$, 400 MHz)



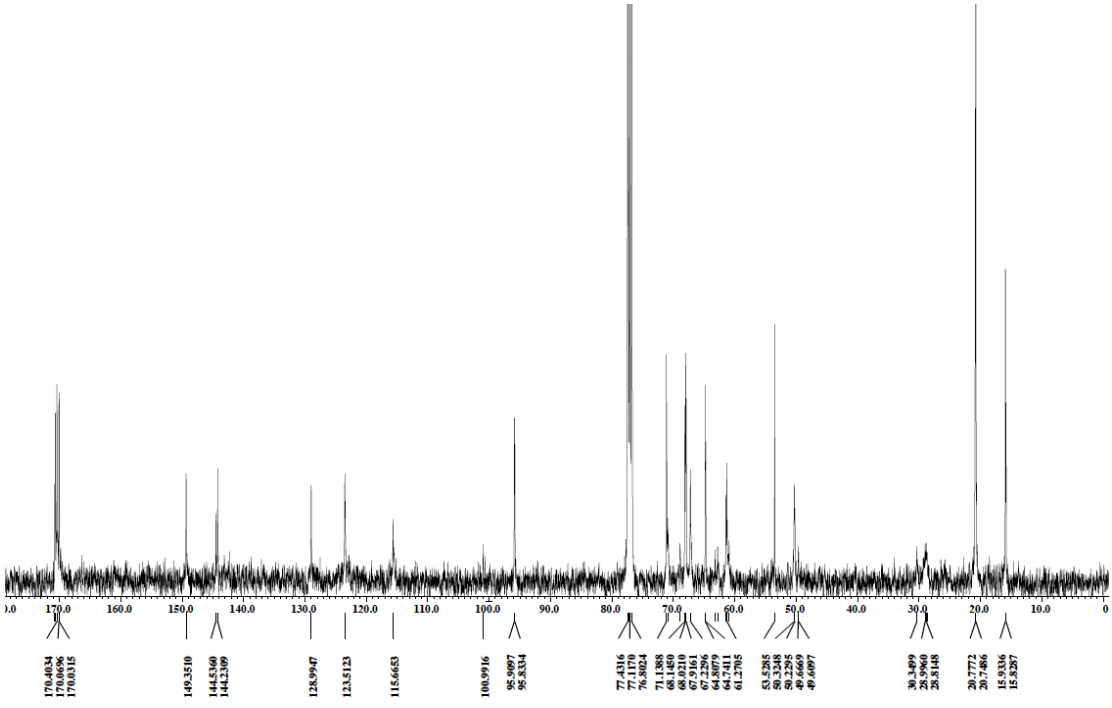
^{13}C NMR spectrum of compound **16** ($CDCl_3$, 100 MHz)



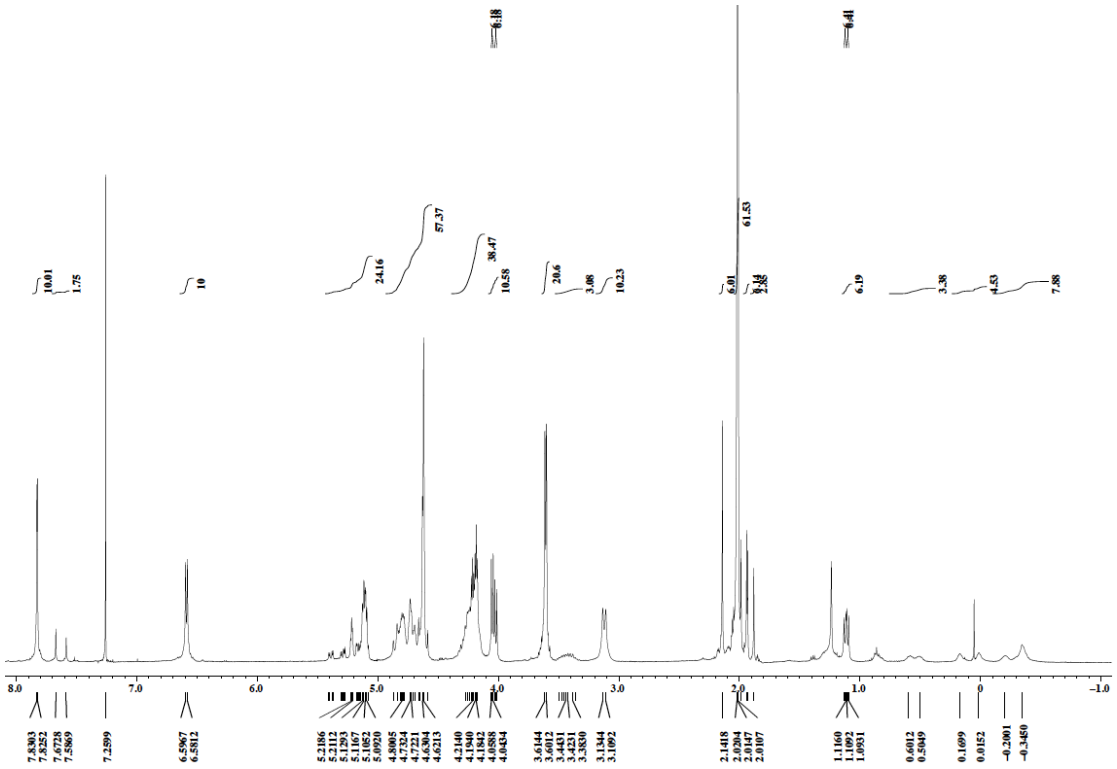
^{1}H NMR spectrum of compound **17** ($CDCl_3$, 400 MHz)



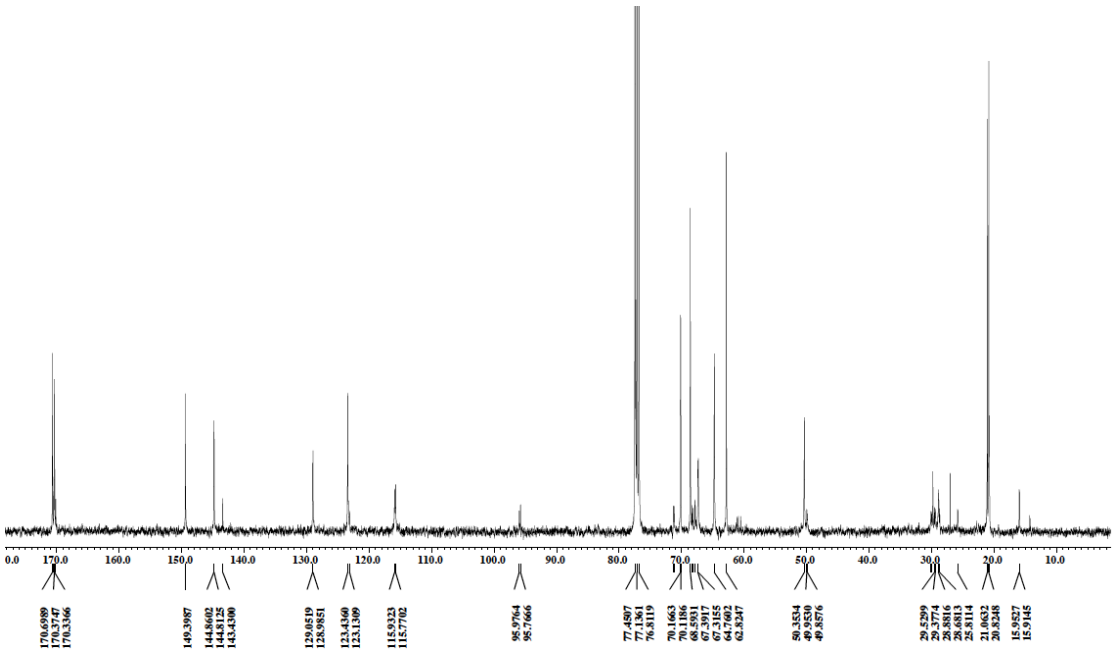
^{13}C NMR spectrum of compound **17** ($CDCl_3$, 100 MHz)



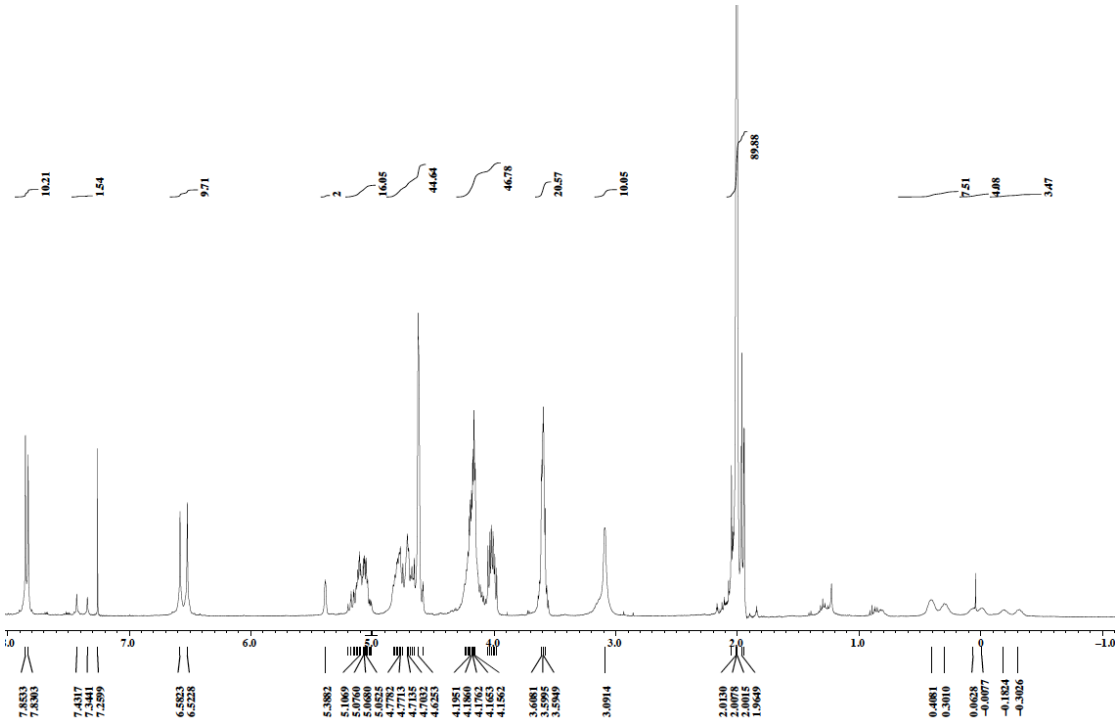
^{1}H NMR spectrum of compound **18** ($CDCl_3$, 400 MHz)



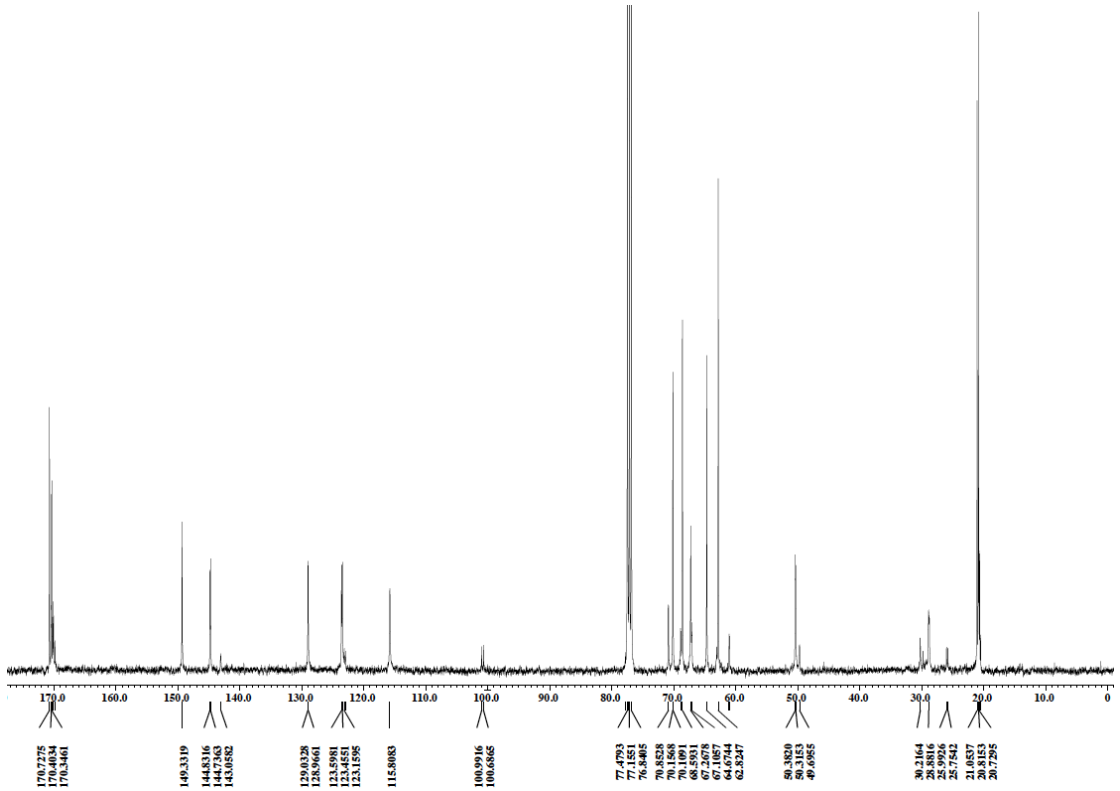
^{13}C NMR spectrum of compound **18** ($CDCl_3$, 100 MHz)



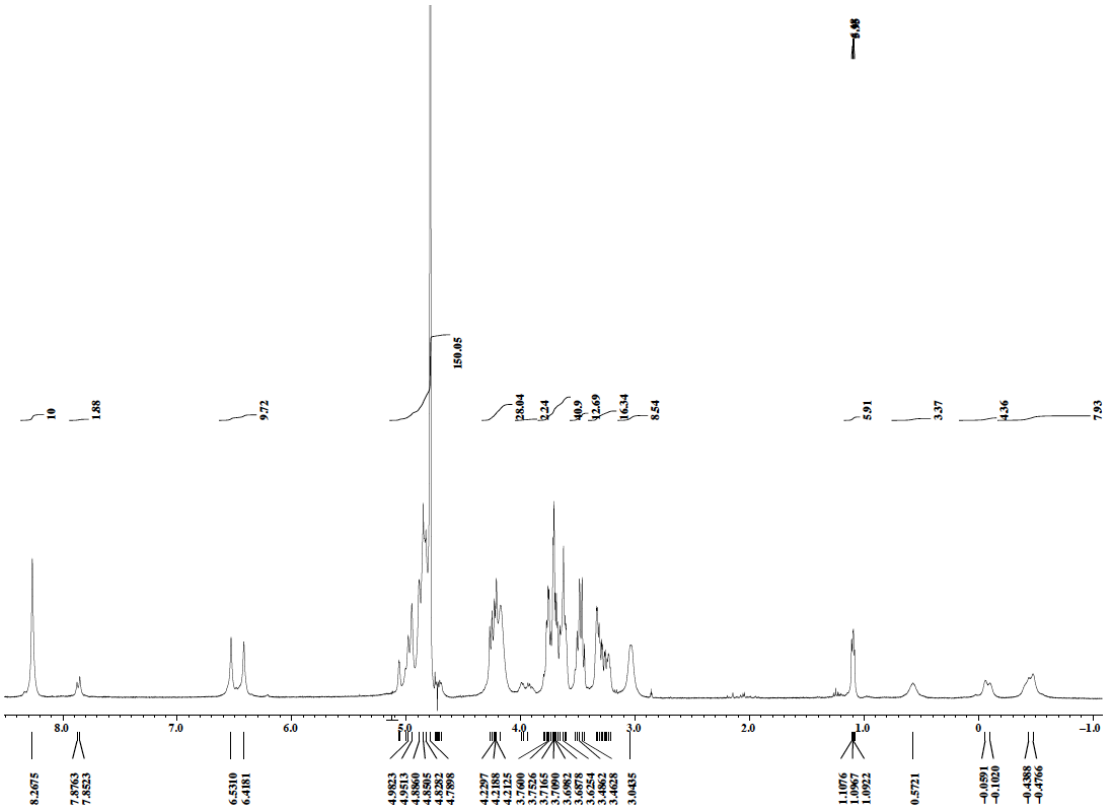
^{1}H NMR spectrum of compound **19** ($CDCl_3$, 400 MHz)



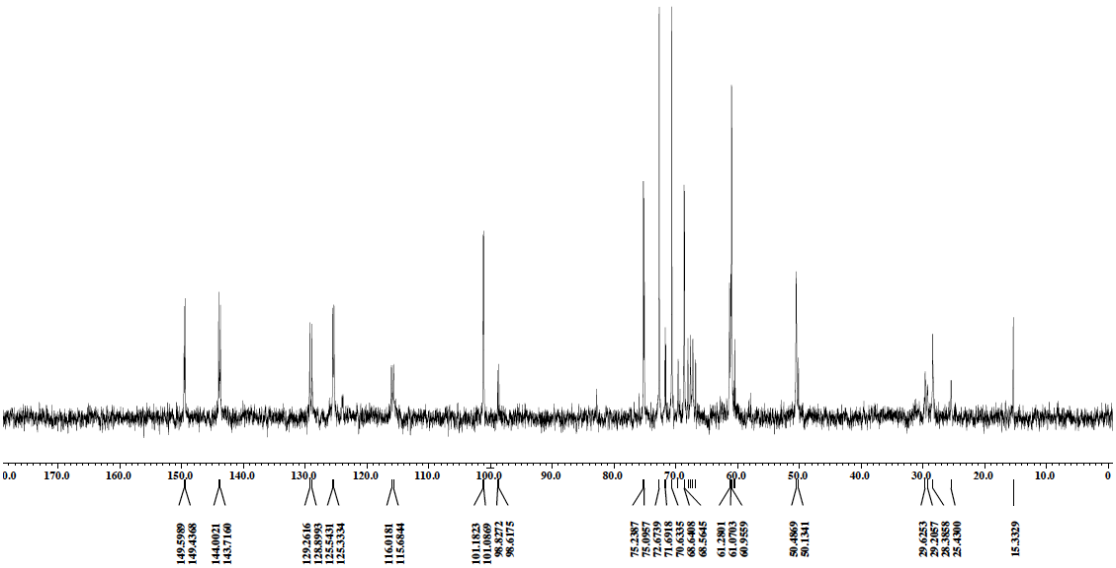
^{13}C NMR spectrum of compound **19** ($CDCl_3$, 100 MHz)



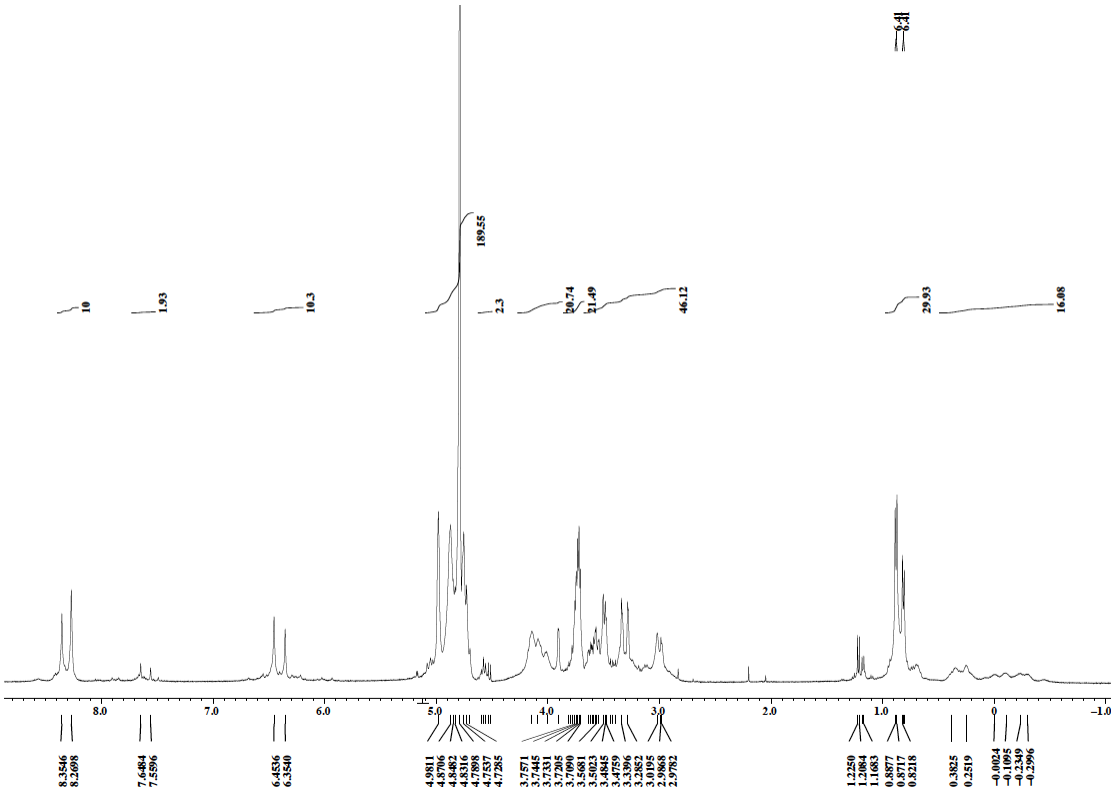
^{1}H NMR spectrum of compound **20** (D_2O, 400 MHz)



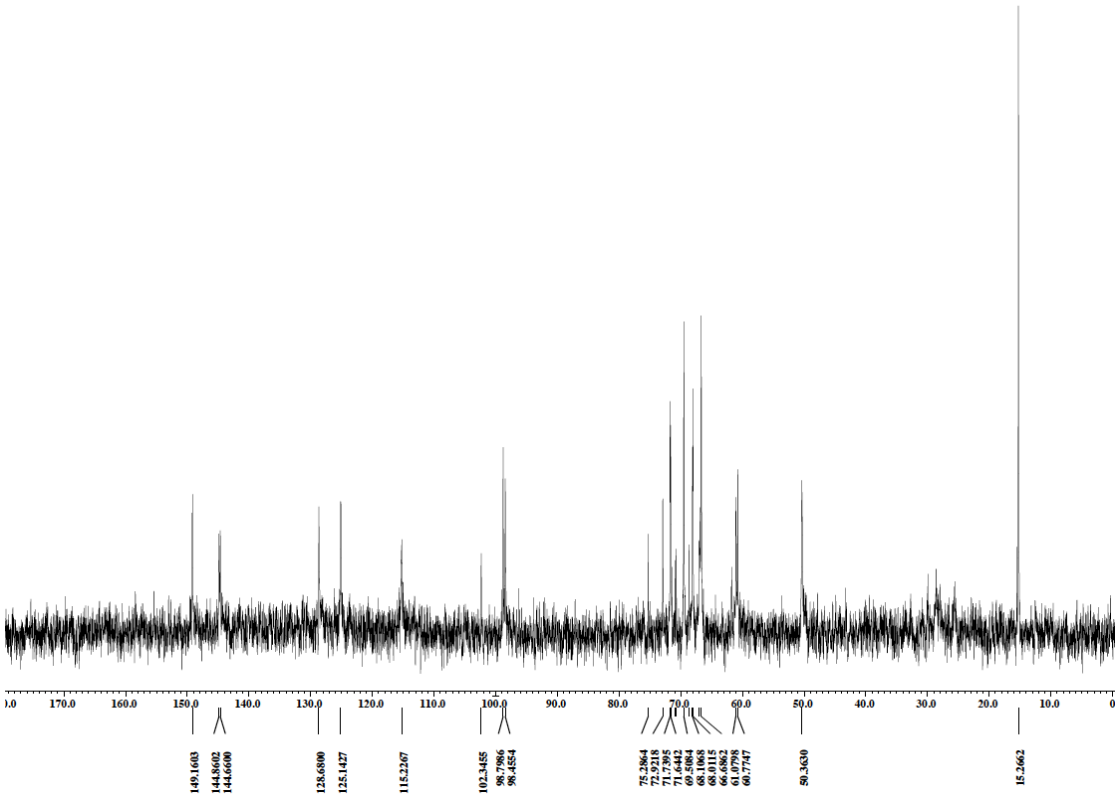
^{13}C NMR spectrum of compound **20** (D_2O, 100 MHz)



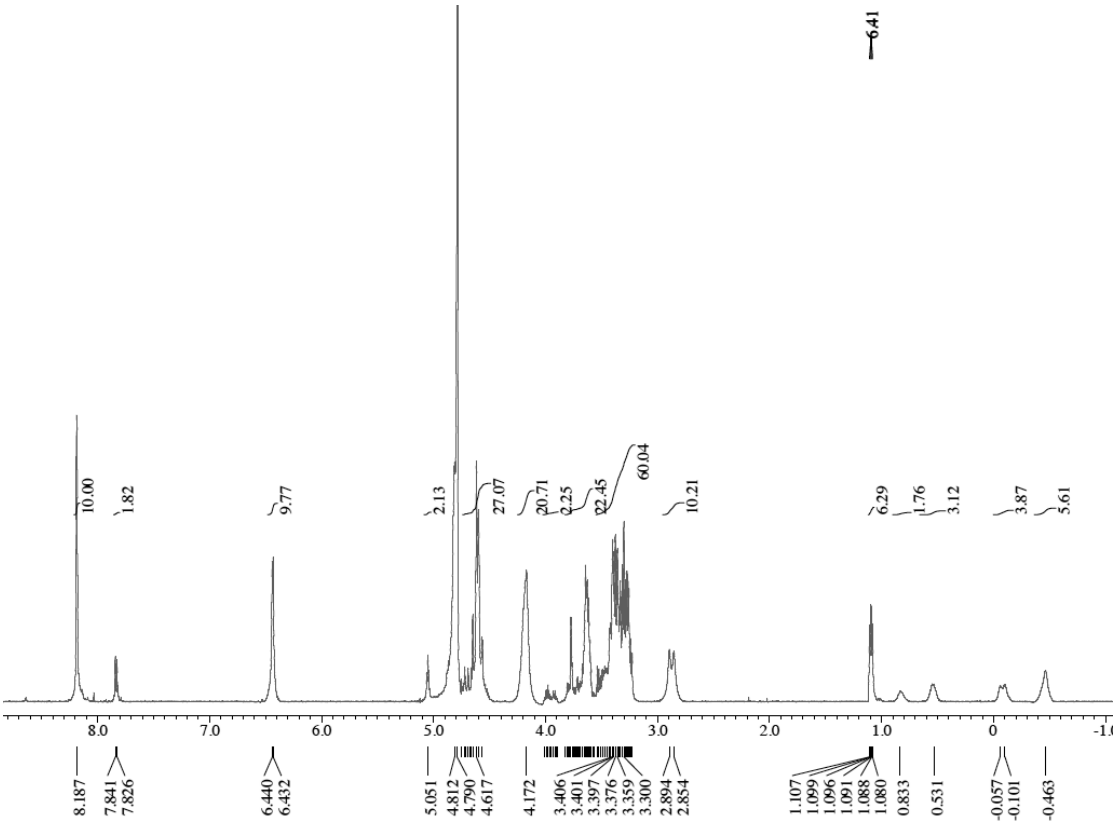
^{1}H NMR spectrum of compound **21** (D_2O, 400 MHz)



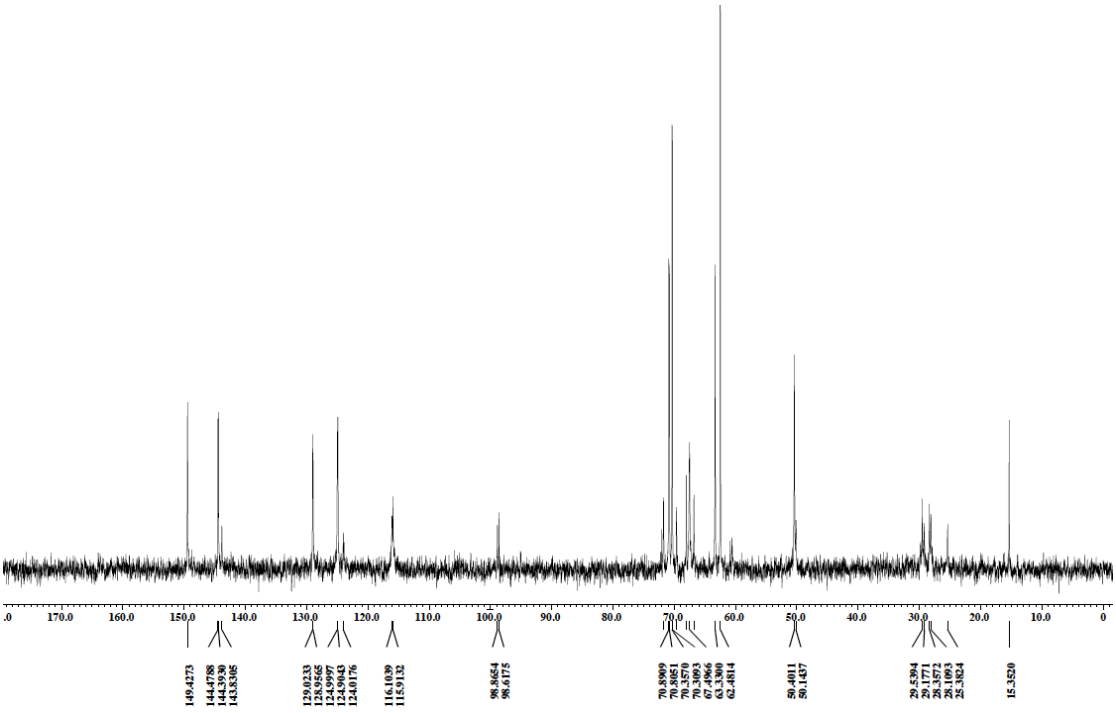
^{13}C NMR spectrum of compound **21** (D_2O, 100 MHz)



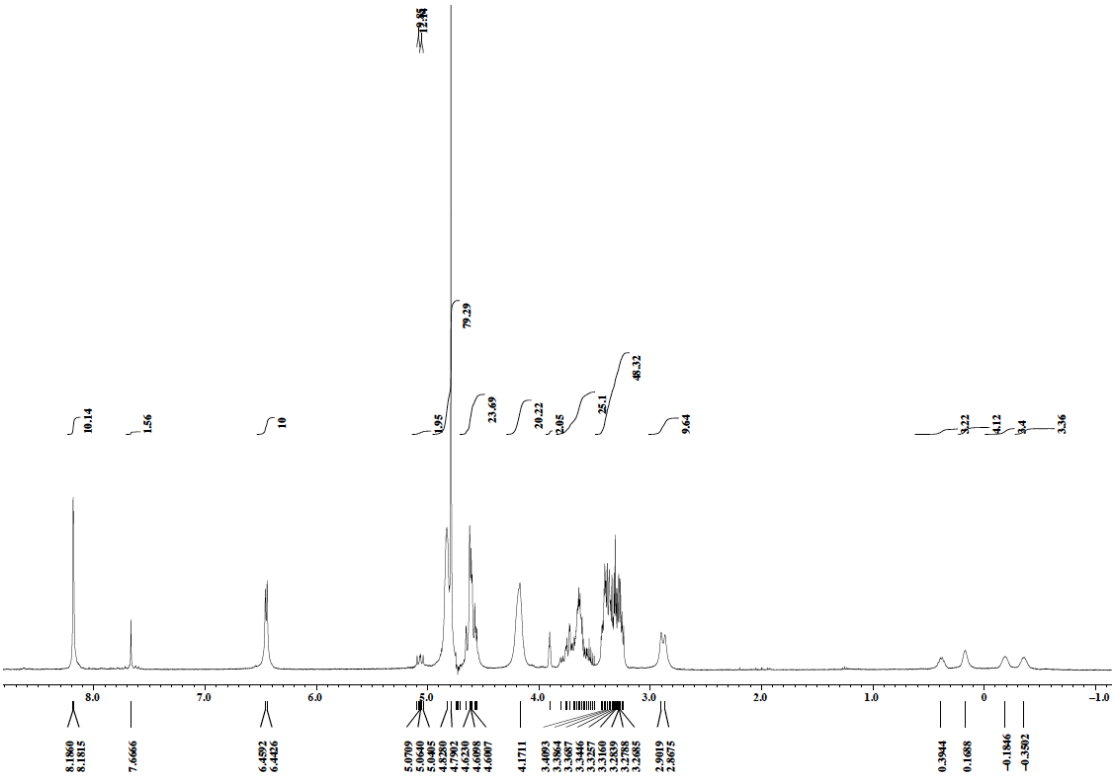
^{1}H NMR spectrum of compound **22** (D_2O, 400 MHz)



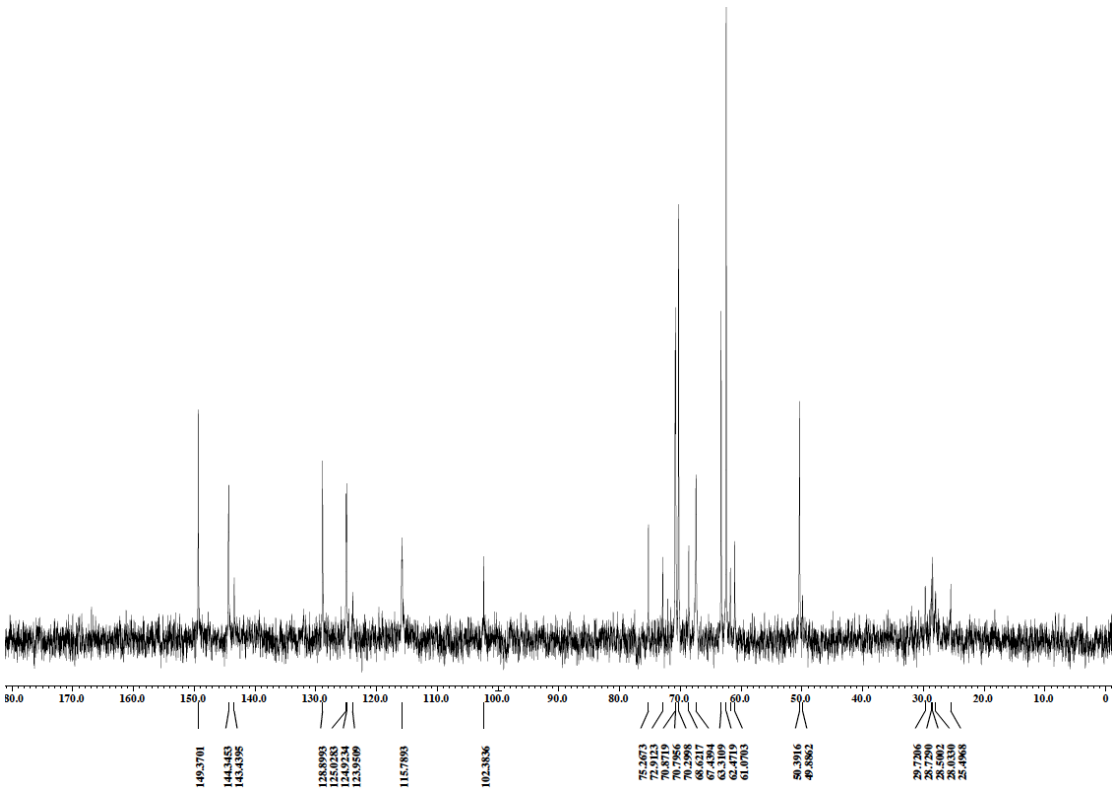
^{13}C NMR spectrum of compound **22** (D_2O, 100 MHz)



^{1}H NMR spectrum of compound **23** (D_2O, 400 MHz)

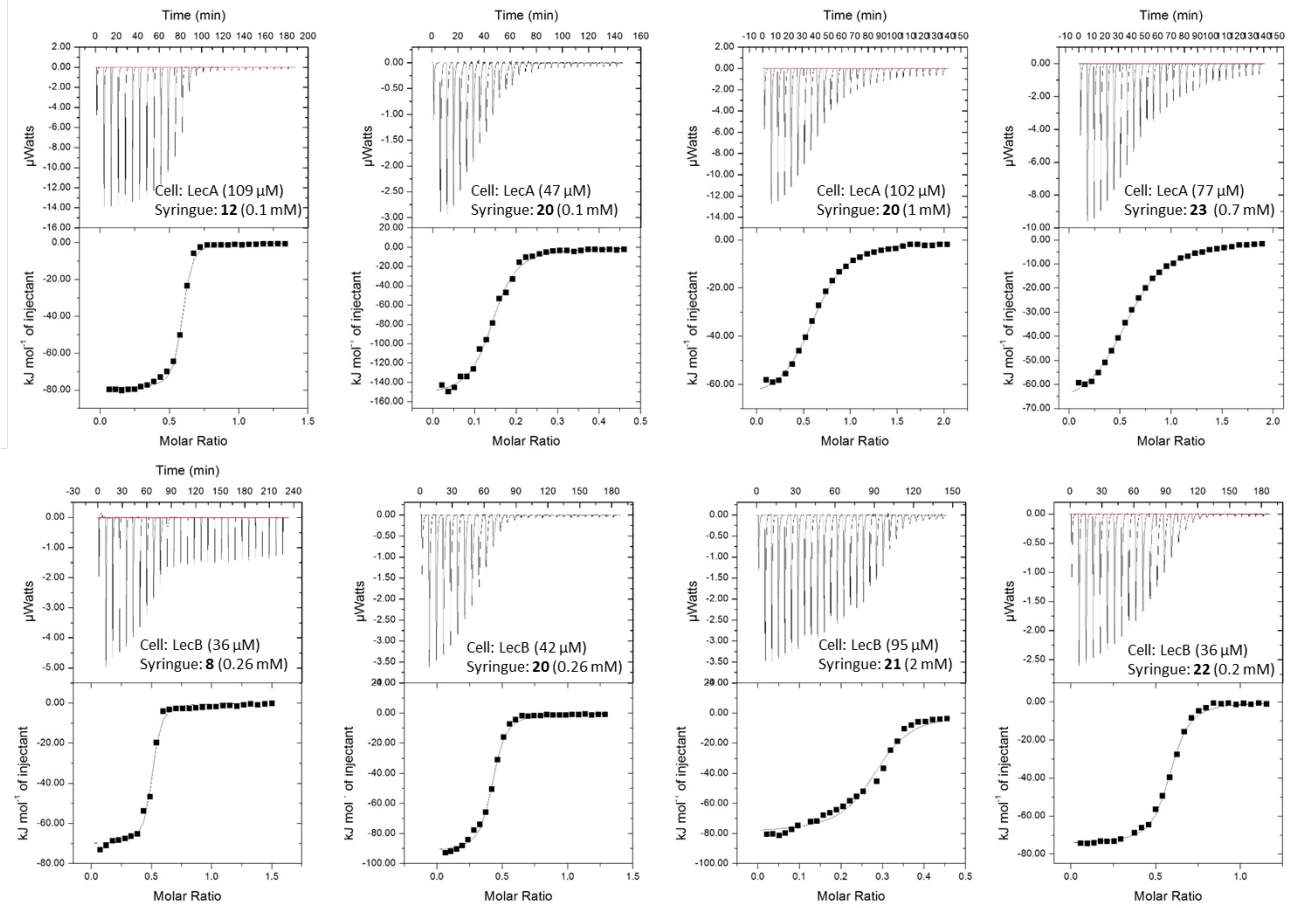


^{13}C NMR spectrum of compound **23** (D_2O, 100 MHz)



ITC measurements

Recombinant LecA and LecB were produced in *Escherichia coli*, purified by affinity chromatography, dialyzed and liophylized as previously described.[7] ITC experiments were performed with a VP-ITC isothermal titration calorimeter (Microcal- Malvern). The experiments were carried out at 25 °C. Lectins and all ligands were dissolved in the same buffer composed of 0.1 M Tris with 0.03 mM $CaCl_2$ at pH 7.5. The protein concentration in the microcalorimeter cell (1.447 ml) varied from 20 to 100 µM. A total of 30 injections of 13 µl of sugar solution at concentrations varying from 0.2 to 1 mM were added at intervals of 5 min whilst stirring at 310 rev./min. Control experiments performed by injection of buffer into the protein solution yielded insignificant heats of dilution. The experimental data were fitted to a theoretical titration curve using Origin software supplied by Microcal, with ΔH (enthalpy change), K_a (association constant) and n (number of binding sites per monomer) as adjustable parameters. Dissociation constant (K_d), free energy change **(**ΔG) and entropy contributions ($T\Delta S$) were derived from the previous ones.



Selected sensorgram and integration with best fit for each compound interacting with lectins.

References

[1] K. Buffet, E. Gillon, M. Holler, J.-F. Nierengarten, A. Imberty, S. P. Vincent, *Org. Biomol. Chem*. **2015**, *13*, 6482-6492.

[2] J. R. Thomas, X. Liu, P. J. Hergenrother, *J. Am. Chem. Soc.* **2005**, *127*, 12434-12435.

[3] T. Ogoshi, K. Kitajima, T. Aoki, S. Fujinami, T.-a. Yamagishi, Y. Nakamoto, *J. Org. Chem*. **2010**, *75*, 3268-3273.

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